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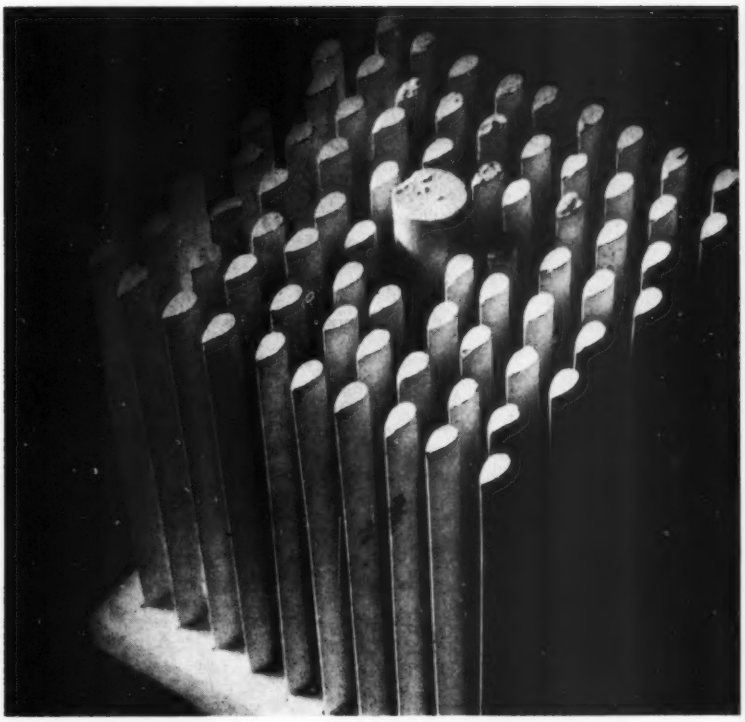
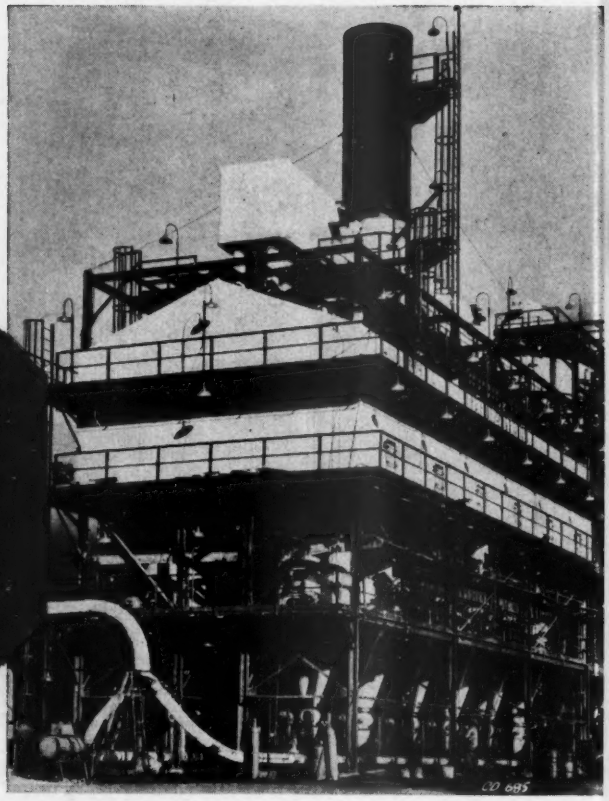
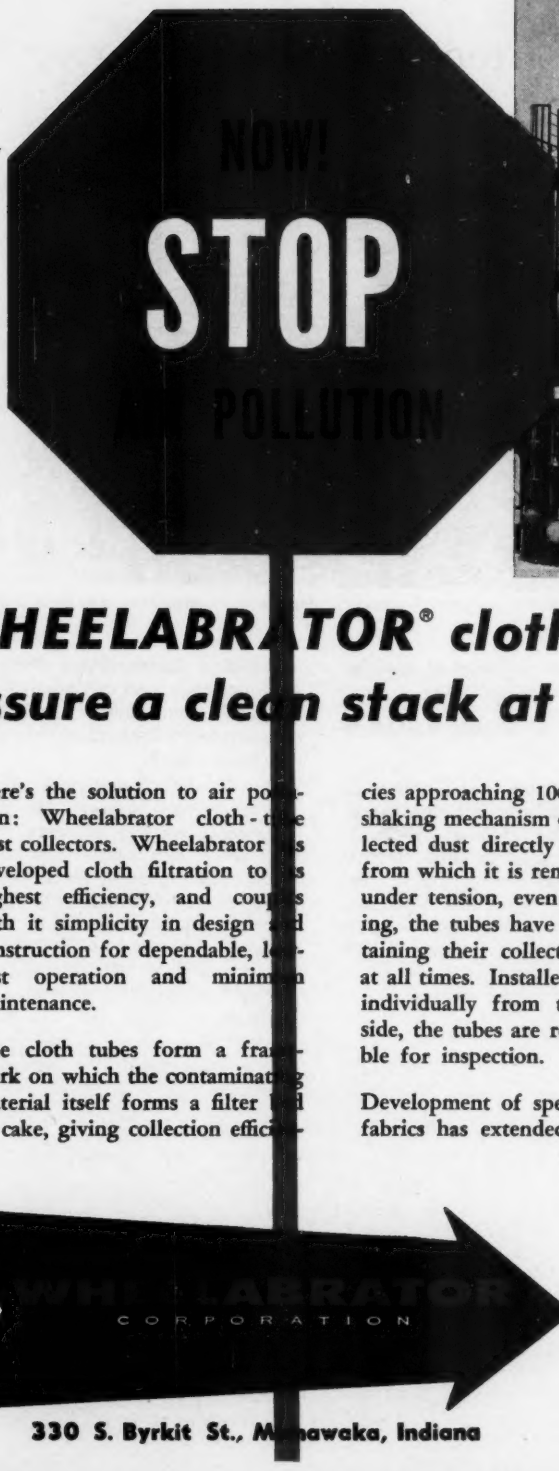


Cross Section of a Catalytic Oxidation Unit
(See Page 182)

November 1957
Vol. 7, No. 3





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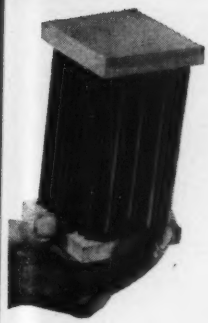

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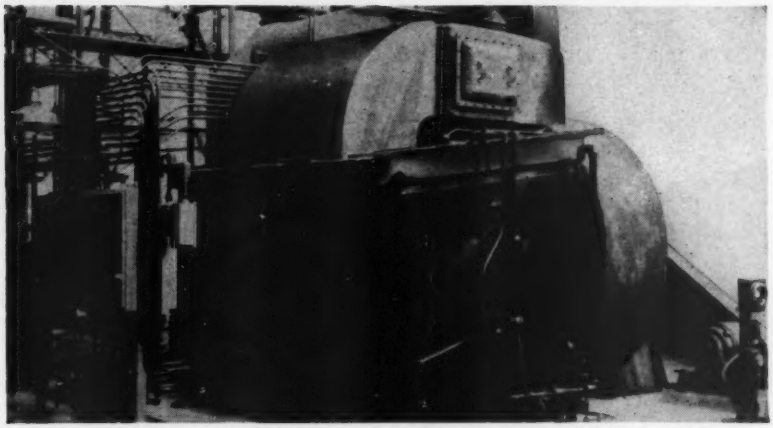

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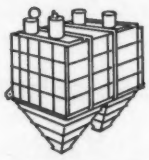

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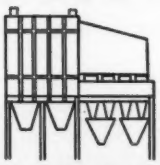

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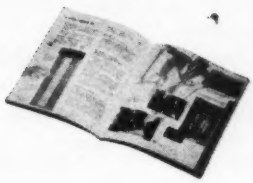

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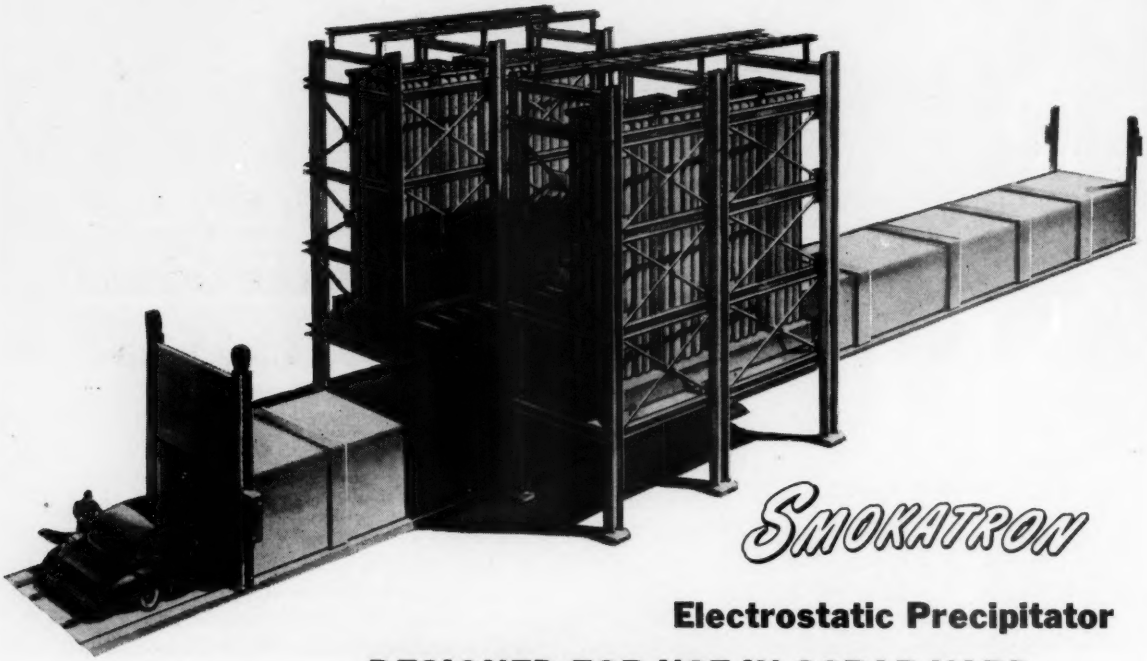

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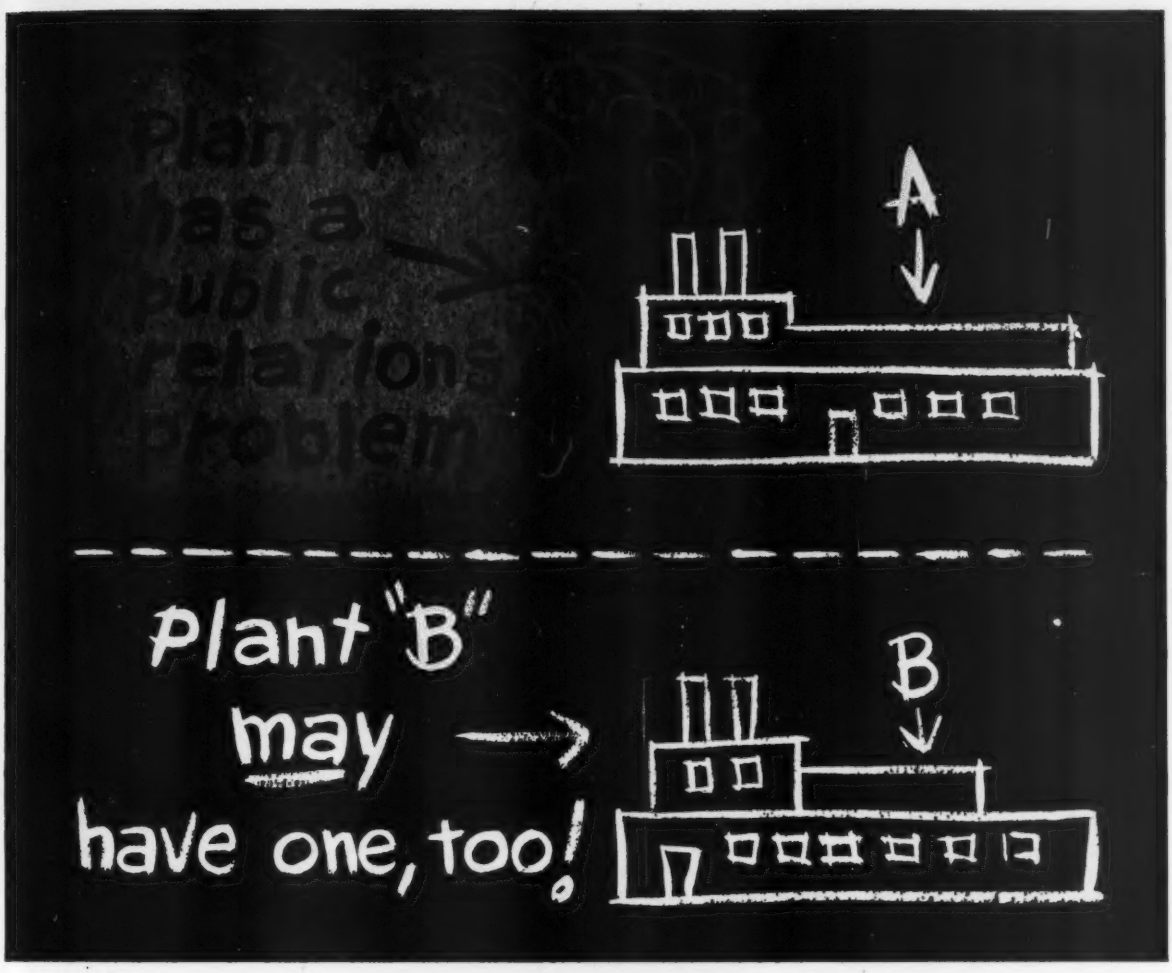

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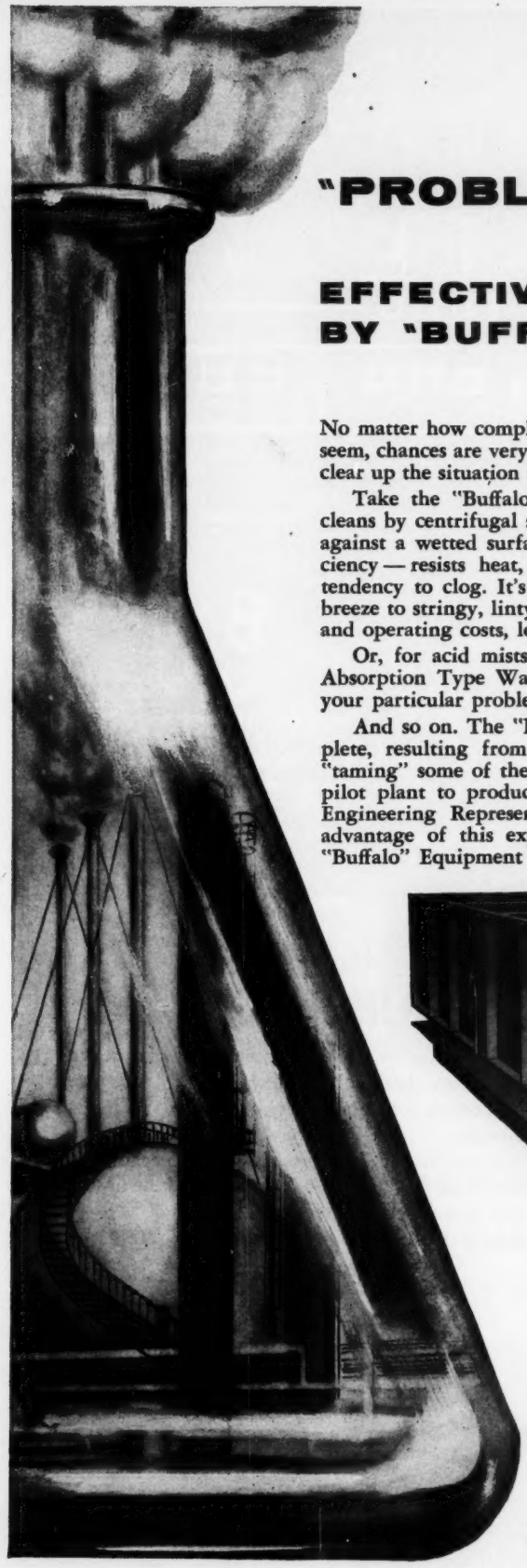

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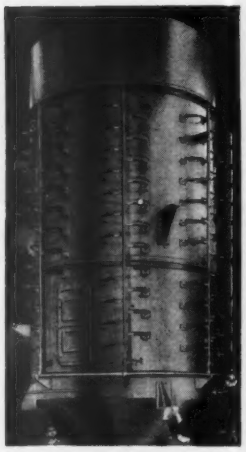

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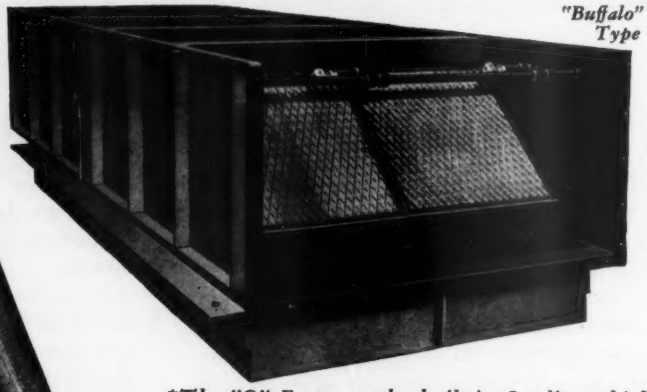

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JOURNAL OF THE AIR POLLUTION CONTROL ASSOCIATION

(Formerly "Air Repair")

A QUARTERLY JOURNAL DEVOTED TO AIR PURIFICATION

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November 1957 **Vol. 7, No. 3**

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The Editor welcomes writers interested in air pollution problems and encourages them to use the pages of this journal for the expression of their opinions. But neither he nor the Association assumes responsibility for the validity of the opinions expressed herein.

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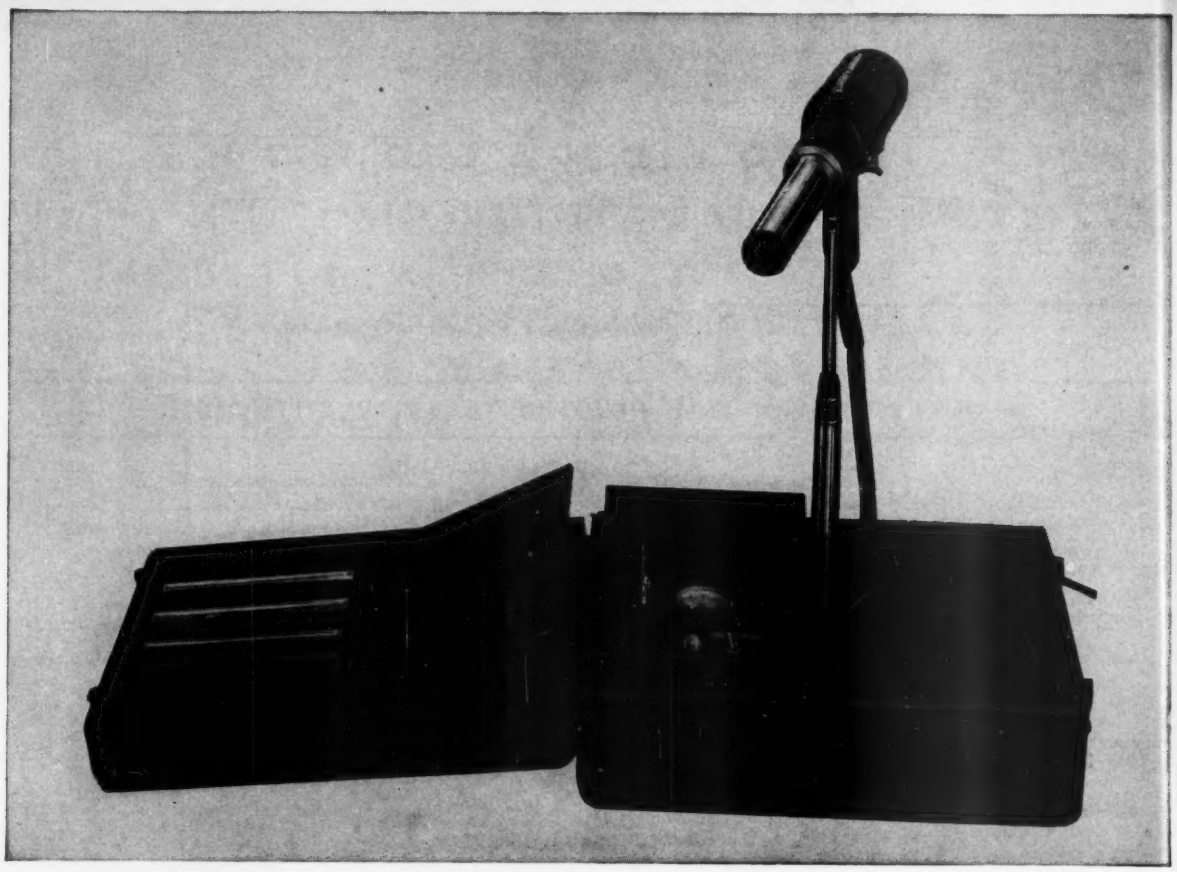

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The ASHAE Air-Borne Dust Survey*

K. T. WHITBY, A. B. ALGREN, R. C. JORDAN AND J. C. ANNIS

University of Minnesota

Minneapolis, Minnesota

Within the last decade numerous airborne dust surveys have been made in connection with industrial health and air pollution studies. A study of these surveys shows that they have yielded only limited data on the physical properties of airborne dusts that have a bearing on their removal by air cleaners.

Thus when the cooperative research project on rating and testing methods for air cleaners for occupied spaces was begun, a search of the existing literature revealed that inadequate data existed on which to base the selection of suitable test dusts for simulated air cleaner testing. A limited dust survey was therefore organized, having the following objectives:

(1) Determination of the concentration of airborne dust in typical indoor and outdoor locations by weight and dust spot. An independent measure of the fibrous airborne particles such as lint was also included, because these largely determine the dust holding capacity of many types of filters.

(2) Determination of the volume size distribution of airborne dust. The volume distribution was desired rather than the number distribution obtained by microscope count, because filter life is determined by the volume concentration.

(3) Determination of other physical characteristics which it was thought might have a bearing on air cleaner performance. Some of these are: density, particle shape, porosity of a packed bed of dust and staining power.

(4) Measurement of dust fall at the sampling site. This was desired because the dust fall on indoor surfaces is sometimes the principal nuisance experienced by the housewife.

A study of these objectives within the framework of available funds, facilities and personnel led to development of several new dust sampling and evaluation techniques and the modification of several old ones. The first part of this paper describes the apparatus, procedures and their evaluations and the second part gives the results from the survey. The original survey as reported in this paper is being extended to include a study of the loading characteristics of representative types of filters in typical service.

Sampling Equipment

Pumps

To permit sampling in occupied spaces the small, quiet and inexpensive diaphragm pump used in the A.I.S.I. smoke samplers were used. These pumps were mounted in small wooden boxes lined with glass fibre sound insulating material. Leakage around the actuator gland required monthly calibration against a wet test meter to obtain a $\pm 5\%$ accuracy of the estimated air volume sampled.

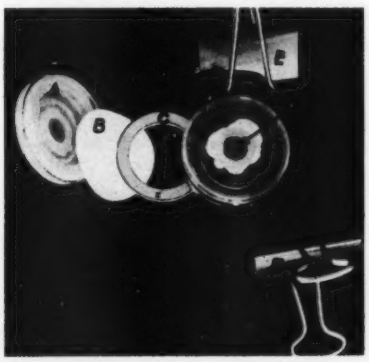

Fig. 1. Exploded view of plastic millipore filter holder.

Filter Holders

The large number of filter holders required led to the development of the inexpensive plastic holders shown in Fig. 1. Designed for the standard unmounted 47 mm. size millipore filters, these holders are made from commercially available 47 mm. size plastic petri dishes.

Part A consists of the bottom of a petri dish with a ½ in. copper tube hose connection cemented in place and a 40 mesh supporting screen cemented to a 47 mm. plastic ring (also available commercially). The ring and screen are cemented in place in the bottom of the dish. B is the millipore filter, C is a gasket ring cut from laminated sponge rubber and leather shoe innersole, D consists of a petri dish top and bottom cemented together with a large hole cut through, F is a dish top with a piece of 170 mesh stainless steel lint screen cemented in place over a ½ in. hole and E are paper clips used to hold the assembly together.

A sampling pump and holders assembled for simultaneous indoor and outdoor sampling is shown in Fig. 2.

Dust Fall Slides

Standard 25 x 75 mm. microscope slides resting on small wood blocks were used for dust fall sampling. Before use these slides were cleaned carefully with detergent and water.

Sampling Procedures

Sampling Locations

Sampling locations were determined by number of factors: Participation was limited to the University of Minnesota and four members of the Technical Advisory Committee on Air Cleaning of the American Society of Heating and Air Conditioning Engineers. Locations in any given city were limited to those readily accessible to the sponsor. Though the sampling pumps were reasonably quiet, locations had to be found where the owners or occupants were willing to tolerate the occasional nuisance of a noisy pump and the

* Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

weekly visits to change sampling media. Thus the number and location of samples taken represents the best compromise that could be made under the circumstances.

Specific locations are discussed with the results.

Typical Sampling Procedure

The light transmission of the clean millipore filters were read before use. The assembled samplers were then placed in operation with the dust fall slide located nearby. Sampling periods varied from 2 days to a week depending on location, dust concentration and the number of filter holders attached to a pump.

The lint screen was omitted by those participants not having a photometer suitable for the evaluation of the lint screen.

Sample Evaluation

Dust Spot

Optical density of the loaded millipore filters was determined with the improved photometer described previously[1] at a 0.75 in. diaphragm opening. These measured optical densities were then used to calculate the staining dust concentration in cohs and for comparison with the optical densities calculated from the sedimentation analysis.

Lint Screen

The pronounced effects of fibrous particles on ventilation filter life made it desirable to incorporate a measure of the concentration of such particles in the survey.

Nomenclature

I_o	= *Light transmission of a clean filter media.*
I	= *Light transmission of a dirty filter media.*
OD	$= \log_{10} \frac{I_o}{I}$
$O.D.D.$	$= \frac{112\,(I_o - I)}{t}$ *(Thousandths of an OD of dust fall/day).*
t	= *time in hr.*
v	= *porosity.*
D_p	= *particle diam. — μ.*
D_{g1}	= *number geometric mean size — μ.*
D_{g2}	= *volume geometric mean size — μ.*
S	= *variance.*
C	= *concentration — gr./tcf.*
K	= *Light scattering coefficient* $= \frac{\text{effective scattering area}}{\text{true particle projected area.}}$

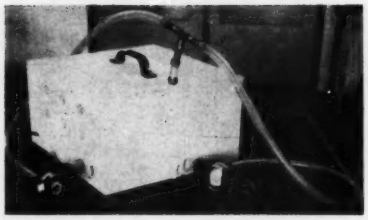

Fig. 2. Sampling pump and filter holders assembled for simultaneous indoor and outdoor sampling.

After considerable study the photometric evaluation of the particles caught on a 1.27 cm.² 170 mesh stainless steel screen placed ahead of the millipore filter was adopted. The small amount of fibrous material normally collected precluded evaluation by weight. Lint screen samples were therefore evaluated with the improved photometer[1]. The optical density was calculated from measurements of the light transmission through the screen with the dust deposit and after thorough washing.

Measurements of both optical density and weight on a special 8 cm./diam., 170 mesh screen by Engebretson[2], on 11 lint samples from typical residential and non-residential locations gave the following relationship between weight and screen light transmission:

$$mg./cm.^2 = 2.52 \log \frac{I_o}{I} \qquad (1)$$

The linear correlation was 0.989 which is surprisingly good. Lint concentrations given in the latter part of this paper are calculated using equation *(1)*. Not all particles collected by the screen are fibrous. Detailed study of mechanism of collection of the screen by Engebretson[2] has shown that inertial impaction of non-fibrous particles above approximately 5 μ in size can account for a substantial fraction of the total collected. Observations on particles collected on the screens during the survey indicate from 50% to 90% of the total can be considered as fibrous. It is therefore believed that this simple lint screen sampling method provides a rough but useful index of the proportion of fibrous particles normally found in airborne dust.

Dust Fall

Dust fall measurement by the use of jars placed out of doors has been standard for many years. Microscope evaluation of dust fall on microscope slides has been used by the telephone company. More recently Hemeon[3] has used photomultiplier measurement of light scattered by dust deposits on microscope slides. Though very sensitive this latter technique suffers because of the difficulty of calibration.

For the ASHAE survey a simple rapid method of moderate accuracy was obtained by increasing the sensitivity of the transmission photometer used for dust spot measurements to the point where the deposits could be evaluated by reduction in the light transmission through the slide. Sensitivity was sufficient to measure the dust fall accumulated in one day in a clean location with an accuracy of ±20%.

Since the photometer measures optical density it has been found convenient to define a unit rate of dust fall in terms of optical density. This unit rate has been designated, for convenience, as O.D.D. and is defined as that quantity of dust fall/day which has an optical density of 0.001, thus:

$$1\ O.D.D. = 10^{-3} \log \frac{I_o}{I} \qquad (2)$$

An evaluation of this dust fall measurement technique by Engebretson[2] showed that the O.D.D. — weight/unit area relationship depends somewhat on the angle of acceptance of the measuring photocell. At a semi-angle of acceptance of 16°, evaluation of samples from 6 representative locations gave the following relationship. Variance was 7%.

$$\log_{10} \frac{I_o}{I} = O.D. = 1.88\ mg./cm.^2 \qquad (3)$$

$$1\ O.D.D. = 1.66\ tons/sq.\ mile\ /\ Month \qquad (4)$$

Particle Size Analysis

Because of the extremely broad size range and variable character of airborne dusts there exists no single size analysis method which can be used to obtain satisfactory accuracy over the entire range from about 0.02 to 50 μ. For this study it was desired to measure or calculate the volume and area size distributions. The volume distribution was used because the volume of airborne dust determines filter life and the area distribution because this is related to the soiling power of the dust[4].

Choice of the centrifuge sedimentation analysis method[5] as the primary method was determined by a number of considerations. Among these were, availability of the equipment, speed, convenience and reasonable accuracy over the 0.3 to 25 μ size range of primary interest. A lim-

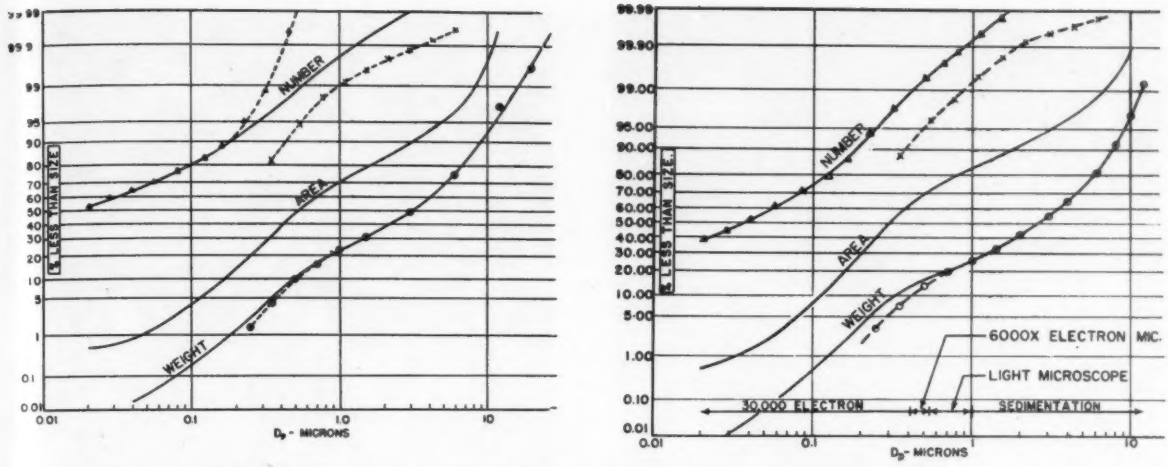

Fig. 3. Typical airborne size distributions from combined light and electron microscope and sedimentation data. Measured by △-Electron microscope, X-Light microscope and O-sedimentation. Left Sample, HA-1, Right Sample, HA-3.

ited number of analyses were made with the light and electron microscope to supplement and check the sedimentation data. Also a few comparisons of sedimentation data with results obtained by other investigators with the jet impactor, particle counter and parallel plate air settling chamber were obtained.

Light Microscope Size Analysis

The light microscope size analysis procedure used has been described previously[4]. Dust samples are collected on hydrosol type millipore filters and are counted and measured using a Porton type reticule at high magnification. The equivalent of 10,000 to 15,000 particles were counted by a multistage procedure.

Electron Microscope Size Analysis

Through the courtesy of Mr. J. Sayer and Mr. M. Jacoby a procedure for taking good electron microphotographs of millipore filter collected samples of airborne dust was developed and several samples thoroughly analyzed. The procedure is briefly as follows:

A 500 to 10,000 Å carbon film is evaporated onto the surface of the millipore filter. The millipore filter is then dissolved away and the carbon film containing the embedded particles is deposited on a grid. Typical photographs of dust sampled in the laboratory are shown in Fig. 4.

Multistage counts on from 3 to 5 photographs enlarged 12,000 to 30,000 times are then made by comparison with black circles having diam. ratios equal to the $\sqrt{2}$. To increase the probability of seeing the larger particles without resorting to an excessive number of photographs, counts on millipores having both high (0.4) and low (0.04) optical densities or on photographs at different magnification were used. The ratios of the measured optical densities can then be used to combine the counts.

Because of the limited number of size analyses made using the electron microscope, only limited conclusions as to its accuracy and usefulness can be made. The time consuming nature of the count procedures and severe sampling problem probably make it mandatory to combine the electron microscope data with light microscope or preferably sedimentation analysis if misleading results are to be avoided. The good agreement between calculated and measured O.D.'s shown in Table III indicates that the carbon film replication technique does account for most of the particles. However, further comparisons with thermally precipitated dust samples are needed to accurately determine the loss of very fine particles (0.01 to 0.1 μ).

Centrifuge Sedimentation Analysis Procedure

The procedure used is essentially that described previously[2, 4, 5]. It is briefly as follows. A millipore filter containing between 0.3 and 1.0 mg. of dust is dissolved in acetone in a 40 ml. centrifuge tube using moderate stirring. The suspension is then centrifuged at 3000 RPM for 1 hr. to precipitate the particles, and the supernatant liquid syphoned off. The dust is resuspended in 1 ml. of feeding liquid consisting of approximately 15% Naphtha — 85% Acetone. This suspension is then floated as a layer on a pure acetone sedimentation liquid and the size analysis carried out by the previously described techniques.

Evaluation of the Centrifuge Sedimentation Procedure

Because of the use of a sedimentation method for the analysis of airborne dusts may be seriously questioned, a rather thorough evaluation of its limitations and probable accuracy was made. The most important considerations and a summary of their evaluations are as follows.

1. Dispersion. The question arises as to whether the sedimentation particle size corresponds to that existing in the air. Throughout the survey the measured optical densities of the loaded millipore filters were compared with the optical density calculated from the sedimentation size distribution and sediment volume by the method described earlier[4]. De-

TABLE I

Sediment Column Porosities for Several Dusts

Dust	D_{gs}	No. of samples	Assumed density	Porosity p	S %
Atmospheric	3.0	13	2.1	.67	54
Arizona Rd. Dust	2.0	8	2.7	.55	
Precipitated Carbon Black	4.5	6	2.1	.88	

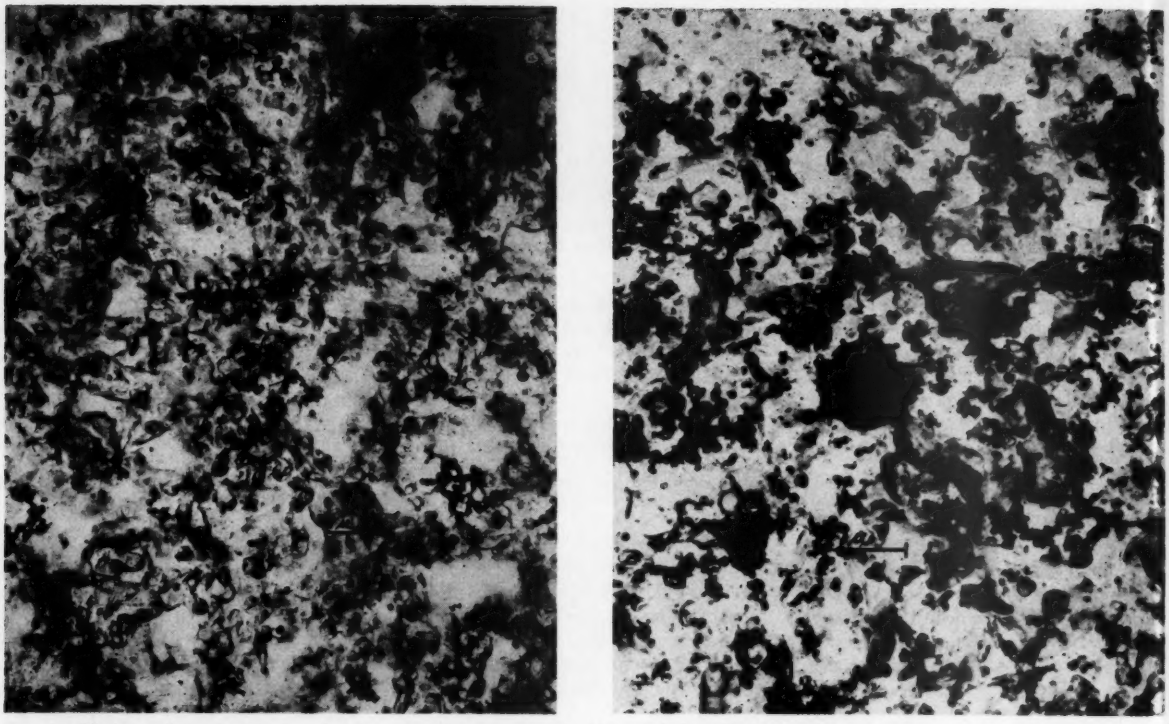

Fig. 4. Electron photomicrographs of millipore collected airborne dust. (a) Sample OC-1, Measured OD = .046, (b) Sample HA-1, Measured OD = .094.

tails of this comparison are given later. The overall ratio of measured to calculated O.D. was 1.93. It is believed that perhaps ½ of the difference between 1 and 1.93 is due to the use of an incorrect K value in the computations. The indications from the detailed studies of the measured optical densities of particles on a millipore at different angles of acceptance by Engebretson[2], from some relatively unsuccessful attempt at measuring the K value directly and from comparisons of measured and calculated O.D.'s for combined size analysis such as Fig. 3, are that the K values are higher at larger particle sizes than is predicted by the diffraction theory curve actually used.

It is therefore believed that the observed agreement between calculated and measured O.D.'s indicates that the state of the dispersion during sedimentation above 0.3 μ is essentially the same as that existing on the millipore except possibly, for very large and fragile aggregates.

2. Millipore dust load. It was found that proper dispersion could not be obtained if the millipore filter contained more than about 1 mg. of normal airborne dust. Irreversible agglomeration of the dust on the millipore apparently takes place if an appreciable number of particles touch each other in the dry state. From circumstantial evidence accumulated during the survey, it appears that normal airborne dust particles are often coated with sticky materials which polymerize in the air stream after the particles are deposited on the filter. Predominantly mineral dusts do not exhibit this irreversible behavior.

During the survey dust loads were normally kept below 0.5 mg./47 mm. diam. millipore.

3. Acetone soluble particles. The sedimentation size analysis techniques employed, measure only the acetone insoluble particles. The work of Chambers *et. al*[6] indicates that the average city dust probably contains 15 to 20% acetone soluble particles. It is, therefore, probable that the dust concentrations computed from the sediment heights are about 15% low on the average. The size distributions reported are therefore only those of the acetone insoluble fraction, since all methods of size analysis used destroy the soluble particles before measurement.

4. Sediment column bulk density. Computations of the dust

TABLE II

Composite Size Analysis of Atmospheric Dust

(Sampled Inside University of Minnesota Particle Lab.)

Particle size μ	OC-1 March 1956		HA-1 January 1957		HA-3 January 1957	
	No.	Wt.	No.	Wt.	No.	Wt.
0.02			52	.006	38	.008
0.04	.7		64	.02	52	.03
0.1	7.5	.02	80	.20	75	.5
.4	87	5.6	97.5	7.1	98.9	13.6
1	99	15.0	99.8	23.1	99.94	26
4	99.98	60	99.995	59.5	99.998	66
10	99.9996	90	99.99999	92.5	99.99998	97.0
20		99		99.7		100.0

As a further check on the accuracy of the measured size distributions, the optical densities for the individual and combined distributions were calculated and compared with the measured OD's. These are tabulated in Table III.

concentration depend on the sediment column bulk density which in turn is a function of the true particle density and the sediment porosity.

Acetone displacement measurement of the density of 5 samples of dust taken from electronic air cleaners operating dry in representative locations gave densities ranging from 1.74 to 2.43 gm./cc. with a mean of 2.06. The lowest value was obtained on dust taken from a residential air cleaner. A density value of 2.1 gm./cc. was assumed for all calculations reported in this paper.

Measurements of the porosity of the sediment column in the centrifuge tube were made on 13 samples of atmospheric dust by weighing millipore samples and then determining the sediment height. To obtain greater weighing accuracy, the sediment from a number of the millipore samples was washed from the centrifuge tubes and reweighed in tared aluminum dishes. Results are given in Table I. A value of 0.6 was used for all computations reported in this paper.

For atmospheric dust values of v (where v = porosity), ranged from 0.4 to 0.84 with the highest values being determined on dust from residential samples or from laboratory samples containing a large proportion of carbon aggregates.

5. Sediment column compaction. Some compaction was experienced with samples containing more than a few percent of fibrous particles. Samples taken without a lint screen preceding the millipore filter were poured through a 325 mesh screen while suspended in the feeding liquid in order to eliminate fibrous particles. Thus the sedimentation data reported in this paper is for the minus 325 mesh fraction only.

The effect of compaction during a size analysis is to give a low estimate of the amount of particles below approximately 0.8 μ. This can be seen in Fig. 3.

6. Reproducibility. The variance of the size analysis on 4 simultaneous samples was determined by Engebretson[2] to be: S = 16% at 5th percentile, 9% at 50th percentile, and 17% at the 95th percentile.

Combined Size Analysis

As a check on the sedimentation size analysis method, three complete analyses of millipore dust samples collected in the laboratory were made, using combined light microscope, electron microscope and sedimentation data. Results of these 3 analyses are tabulated in Table II and the later 2 plotted in Fig. 3.

These distributions were computed* using light and electron microscope data below 1 μ and sedimentation data above 1μ. Upper size limits for the light and electron microscope were taken equal to the size where the probability of seeing a larger particle is about equal to 10^{-4}. This limit was chosen because it is impractical to count more than about 10^4 particles even with multistage procedures. Lower limit for the light microscope is determined by the limit of resolution.

The lower limit for the sedimentation analysis as used in the combined analysis, is 1 μ. Actually the useful lower limit is about equal to the size at which the cumulative percent is about equal to the sediment column reading accuracy. For normal airborne dust this is between 0.2 and 0.4 μ.

As a further check on the accuracy of the measured size distributions, the optical densities for the individual and combined distributions were calculated and compared with the measured O.D.'s These are tabulated in Table III.

From Fig. 3 and Tables II and III, it is possible to draw a number of conclusions.

(1) The light microscope can at best give only a poor estimate of the complete size distribution of normal airborne dust. This is shown by the poor agreement between calculated and measured O.D.'s in Table III and the fact that only 0.2 to 0.1% or less of the particles can be seen using practical techniques.

(2) A single stage electron microscope count such as was used on sample HA-1 is inadequate. However, the multistage E M count used on HA-3 (Fig. 3B) appears to give accurate data up to about 1 μ.

(3) The sedimentation method will be most accurate above 1 μ but gives a progressively lower estimate below 1 μ. From Fig. 3 it can be seen this error is not too serious above about 0.4 μ.

(4) Probably the most accurate method would be a combination of sedimentation and electron microscope.

(5) From Fig. 3b, it can be noted that the 99.9% by number of particles below 1 μ accounts for over 90% of the projected area or staining power, but only about 25% of the total volume. This illustrates clearly that the rating of air cleaners by number, dust spot or weight arrestance have quite different meanings.

Dust Survey Results

Sampling Frequency & Location

Dust survey samples were taken by 6 contributing groups in 4 individual cities, *viz:* three in Pittsburgh; one in Louisville; one in Akron; and the University of Minnesota in Minneapolis. The majority of sampling was done in Minneapolis and Louisville, but enough samples were received from the other cities to indicate the amount of variation to be expected between extreme conditions.

The groups took samples in the following locations: inside and outside residences; inside and outside labs and offices; inside industrial plants. The inside locations represented a range of conditions from old downtown-area buildings employing no air cleaning to newly-remodeled, windowless offices with modern air cleaning equipment. Outside sampling was done in areas ranging from commercial districts to clean residential areas.

Unfortunately, it was impossible to maintain continuous or nearly-continuous sampling at any given location throughout a complete year's cycle. Only at the University of Minnesota were enough samples obtained to test for seasonal variations.

Averaging Procedure

All *overall* average values are the result of weighting equally the 3 major location categories — *(1)* inside residences, *(2)* inside labs and offices, and *(3)* outside. This gives twice as much weight to inside locations as to outside, which might be justified on the grounds that a high percentage of the air passing through most ventilation air cleaning systems is recirculated air, but the average values at each location are so similar that any reasonable system of weighting would produce essentially the same results.

The average values *inside residences* were obtained by weighting equally the averages for 3 cities — Louisville, Minneapolis, and Pittsburgh. *Inside labs and offices* averages were computed by giving equal

* Due to the involved nature of this work, it is planned to write a separate paper describing the methods of analysis, theory and computational procedures.

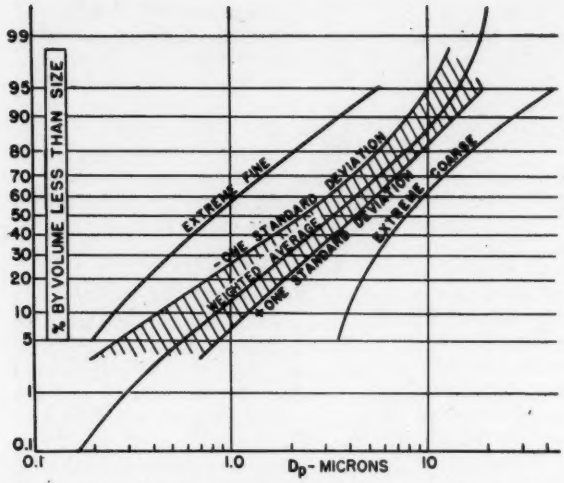

Fig. 5. (Above) Sedimentation size distribution of airborne dust wet-sieved thru 325 mesh screening.

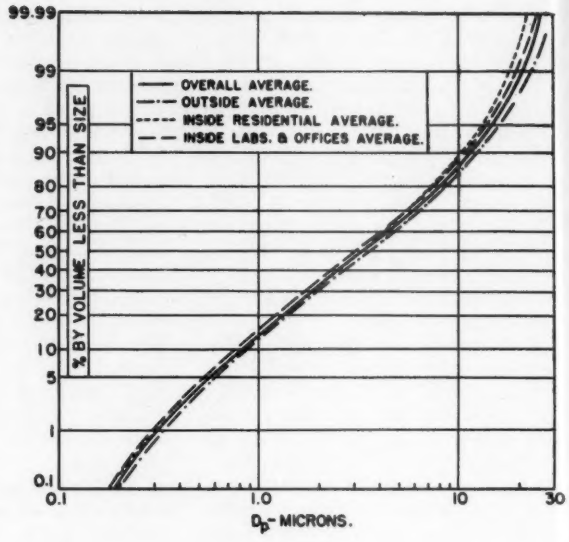

Fig. 6. (Right) Average sedimentation size distributions wet-sieved thru 325 mesh screening for three locations.

weight to the average values for Minneapolis and Louisville. The *outside* average values gave equal weight to averages from 3 cities—Akron, Louisville and Minneapolis—on all items except those pertaining to size distribution. For the 5, 50, and 95 percentile sizes, averages from Pittsburgh were included at equal weight.

Average Dust Properties

Geometric Mean Sizes. The geometric mean size by volume (D_{g3}) of natural airborne dust, was found to vary with location, and displayed a range of values at any given location. The mean size was 3.25 μ, with a 30% variance (S). Inside residences, D_{g3} was 3.17 μ (S = 24%).

A breakdown of this data is contained in Table IV. The south Minneapolis samples were obtained in two separate, but closely-located homes in the extreme southern part of the city. The Louisville sampling was done in three homes. The overall average of D_{g3} = 3.17 $\pm$24% covers a range which includes all of the individual averages shown.

Inside labs and offices, D_{g3} = 3.01 μ (S = 29%). Table II contains the more detailed data from which this average was obtained. Offices and laboratories were combined as one category because of the similarity of their construction and atmospheres. Both are relatively lint-free and clean, and do not have direct outside entrances.

Outside air had a geometric mean size, by volume of D_{g3} = 3.56 μ (S = 33%). Table IV shows the detailed data.

As noted from the variance, the geometric mean size has considerable spread. The values for inside residences ranged from 1.34 to 4.60 μ and for inside labs and offices from 0.83 to 5.15 μ. For outside air the range was 2.69 to 7.60 μ.

At a confidence level of 95% or higher, the average inside residential and inside labs and offices means are equal, but each of these varies significantly from the outside average.

Character of Cumulative Size Distribution Curve. In general, the cumulative size distribution curve is bimodal. An overall average curve, weighting equally the 3 major classes of location, is as shown in Fig. 5, with 5%, by weight, smaller than 0.56 μ, 50% smaller than 3.25 μ, and 95% smaller than 14.3 μ. Fig. 5 includes, additionally, the curves corresponding to plus and minus one standard deviation, and the extreme distributions found. The distributions for each of the 3 major locations, shown in Fig. 6, are very similar to the overall average distribution and warrant no further explanation. The size distributions for individual

TABLE III
Comparison of Measured and Calculated Optical Densities for Atmospheric Dust Samples HA-1 and HA-3

Distribution	Measured O D	Calculated K = 1	Calculated K for Diff. Theory†
Sample HA-1			
Light Mic. Alone	0.094	0.0106	0.0164
Elect. Mic. Alone	0.094	0.0586	0.0654
Sed. Alone	0.417	0.290	0.437
Combined	0.094	0.0706	0.0914
Sample HA-3			
Light Mic. Alone	0.122	0.0115	0.0187
Elect. Mic. Alone	0.122	0.1008	0.0128
Sed. Alone	0.568	0.324	0.460
Combined	0.122	0.115	0.104

†The light scattering coefficient, K, used is that suggested by Davies[4] for opaque particles in a transparent media. No satisfactory data exists for opaque particles on a translucent filter media.

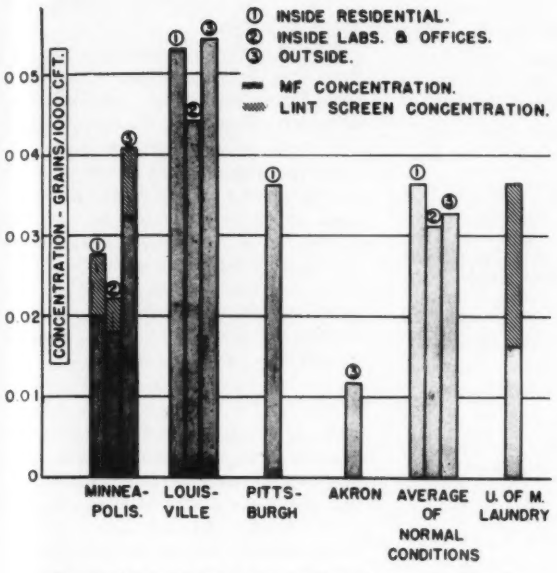

Fig. 7. (Above) Dust concentrations for several locations.

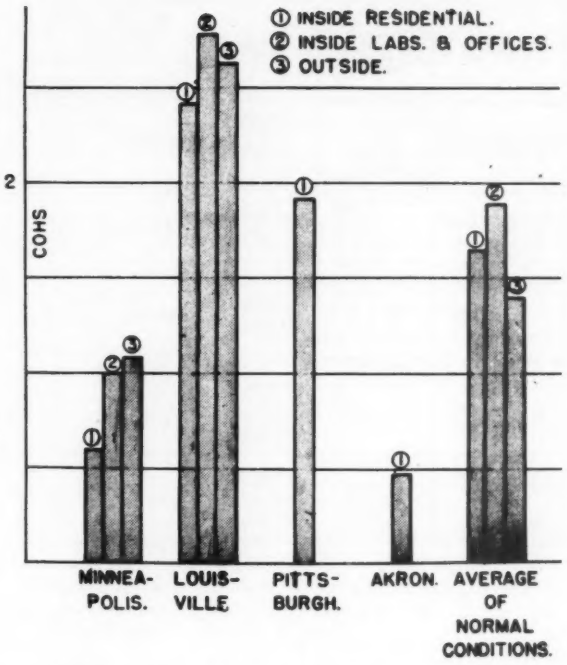

Fig. 8. (Right) Staining concentration.

samples were strongly bimodal, but this characteristic was diminished by successive average processes.

Percentage Lint. Because all of the groups were not equipped to measure the lint concentrations, an overall average is not possible. Considerable information is available, however, from the Minneapolis data.

Inside Minneapolis residences, the lint screen loading constituted an average of 27.6% of the total dust weight. Breaking this average down further, 13 South Minneapolis samples showed an average 27.8%, and 4 Southeast Minneapolis samples had an average of 27.4%.

Dust samples taken inside Minneapolis labs and offices had an average lint screen loading of 17.2%, by weight. Considering the 24 office samples alone, offices had 16.6%. The 41 lab samples had an average of 18.0%.

Air outside the Minneapolis lab contained 21.5% and air outside south Minneapolis residences contained 16.4%.

TABLE IV

Median Size Inside Residences

	No. samples	D_{gs} — μ	S—%
All residential	26	3.17	24
All Minneapolis residential	17	3.31	23
South Minneapolis	13	3.41	17
Southeast Mpls. Apt.	4	3.00	38
Louisville residential	6	2.64	27
Pittsburgh residential	3	3.57	9

Median Size Inside Labs and Offices

	No. samples	D_{gs} — μ	S—%
All samples	67	3.01	29
Minneapolis Labs & Offices	64	2.69	37
Minneapolis Labs	41	2.35	35
Minneapolis Offices	24	3.30	31
Louisville Labs & Offices	3	3.32	16

Median Size — Outside Air

	No. samples	D_{gs} — μ	S—%
All samples	40	3.56	33
Minneapolis (all)	23	4.31	28
Minneapolis Lab	13	4.09	30
Minneapolis South Residences	8	4.95	20
Louisville (all)	9	2.65	21
Louisville Lab & Office	3	3.10	21
Louisville Residential	6	2.43	13
Akron (Residences & Lab)	5	2.82	10
Pittsburgh	3	4.47	22

Louisville mean size of 2.65 μ, it will be noted, was considerably less than Minneapolis average mean of 4.31 μ, and even further from the south Minneapolis residential mean of 4.95 μ.

Average Concentrations

The airborne dust retained on the millipore filter had an overall average concentration of C = 0.0335 gr./tcf (S = 77%). No overall lint-screen concentration is possible for reasons explained previously. Fig. 7 illustrates the differences in concentrations for the 3 classes of location between cities, plus information on an unusual location.

Inside Residences. The average MF (millipore filter) concentration inside residences was C = 0.0365 gr./tcf* (S = 85%). Minneapolis residences had an average MF concentration of 0.0200 gr./tcf (S = 67%) and a lint concentration of 0.0076 gr./tcf (S = 80%) for a to-

SHAPE	APPEARANCE	KINDS	% IN DUST BY WT.	
			RANGE	AVE.
SPHERICAL		SMOKES POLLEN FLY ASH	0-20	10
IRREGULAR CUBICAL		MINERAL CINDER	10-90	40
FLAKES		MINERALS EPIDERMIS	0-10	5
FIBROUS		LINT PLANT FIBER	3-35	10
CONDENSATION FLOCCS		CARBON SMOKES FUMES	0-40	15

Fig. 9. Airborne dust particle shapes.

tal of 0.0276 gr./tcf (S = 61%). The south Minneapolis residential samples, taken alone, averaged 0.0162 gr./tcf MF dust (S = 25%), 0.0062 gr./tcf lint (S = 57%) and 0.0244 gr./tcf total (S = 34%).

Louisville residences had an average MF concentration of 0.0531 gr./tcf (S = 86%) while the Pittsburgh MF concentration was 0.0364 gr./tcf (S = 21%).

Inside Labs & Offices. The average MF concentration inside labs and offices was 0.312 gr./tcf (S = 70%). The Louisville MF samples averaged 0.0442 gr./tcf (S = 53%) while the Minneapolis MF average was 0.0183 gr./tcf (S = 52%). In Minneapolis an additional 0.0038 gr./tcf (S = 89%) was measured as lint, for a total concentration of 0.0221 gr./tcf (S = 56%).

Outside Air. Samples of outside air had an average MF concentration of 0.0328 gr./tcf (S = 71%). Akron MF concentrations averaged 0.0118 gr./tcf (S = 45% while Louisville had 0.0543 gr./tcf (S = 42%) and Minneapolis had 0.0324 gr./tcf (S = 42%). In addition, Minneapolis had a lint concentration of 0.0085 gr./tcf (S = 59%) for a total concentration of 0.0409 gr./tcf (S = 27%).

Measured Cohs

The measured coh values for the principal locations and cities are as shown in Fig. 8. The most significant fact is that the variation between cities is much more pronounced than the variation between locations within any one city. The locational variations within each city are of doubtful significance.

Ratio of Measured Cohs to Calculated Cohs

The overall average ratio of measured, to calculated cohs was 1.93 (S = 46%), corresponding to a mean size of 3.25 μ. The inside residential ratio was 1.82 (S = 48%), corresponding to $D_{g3} = 3.17\ \mu$, while the value inside labs and offices was 2.19 (S = 47%) for $D_{h3} = 3.56\ \mu$.

As a further check on the effect of size distribution on the ratio of measured to calculated cohs, the average ratio of all samples with a mean size less than 2 μ was compared to the average ratio for samples with mean diam. greater than 4 μ. The *under 2-μ* samples yielded an average $D_{g3} = 1.58\ \mu$ and a ratio of measured to calculated cohs of 1.43. The *over 4-μ* samples had a D_{g3} of 4.83 μ and a ratio of 2.68. The difference between these ratios was significant at a 99.9% confidence level.

Dust Fall

Measurements of the atmospheric dust fall were made only at Minneapolis. The respective values are given in Table V.

The variation between labs and offices was not significant at a 95% confidence level, and similarly the variation between residences and *labs and offices* was insignificant. However, the average value for outside samples is significantly different from average of all inside samples. Therefore, it may be concluded that in Minneapolis the dust fall is essentially constant for all normal inside locations, although scattered data indicates significant variations between rooms of a particular house.

Seasonal Variations

A significant season variation in mean dust size was evidenced in samples taken inside the Minneapolis lab, the only sampling location having sufficient year-around data for such an analysis. The year was divided into 2 periods *(1)* the non-heating season from June 1 to August 31, and *(2)* the remainder of the year, September 1 to May 31. The average for the period June 1 to August 31 was $D_{g3} = 1.83\ \mu$ while the remainder of the year had an average of 2.58 μ. This difference in mean sizes was significant at a 95% confidence level.

Significant variations were also noted in millipore filter and lint screen concentrations, for the same location. The MF concentration for the period, June 1 to August 31, averaged 0.0130 gr./tcf (S = 25%), while for the remainder of the year it averaged 0.0175 gr./tcf (S = 34%. This difference was significant at a 95% confidence level. The corresponding lint screen concentrations were 0.0022 gr./tcf (S = 65%) and 0.0042 gr./tcf (S = 42%), respectively. This difference was significant at better than a 99% level.

The bimodal character of the size distribution, referred to previously, was appreciably diminished or nonexistent within experimental accuracy in the majority of summer samples. The summer atmospheric dust, it has been noted has finer distribution, a lower concentration, and a

TABLE V
Dust Fall in Minneapolis

Location	No. of samples	O.D.D.	S—%
1. Inside Labs & Offices	30	0.80	66
Inside Labs	8	0.63	91
Inside Offices	22	0.86	57
2. Inside Residences	12	0.93	56
3. Outside	13	4.92	26

* gr./tcf is grains per thousand cubic feet.

measured to calculated coh ratio closer to unity than the dust existing during the remainder of the year. This may be explained by considering the normal atmospheric dust to consist of two general types of material, besides the lint; a mineral fraction of relatively fine size distribution, and a carbonaceous fraction of relatively coarse distribution. These 2 overlapping distributions would give the bimodal characteristic in the fall, winter, and spring, with the carbonaceous fraction gradually diminishing until an almost unimodal distribution is obtained during the summer. The mineral fraction concentration is believed to remain fairly constant year-around. The lower measured to calculated coh ratio substantiates this theory, because supplementary work has indicated that the principal error in the K values assumed for the purpose of this work, is at the coarse end of the range. Additional evidence is the fact that the summer samples are brown rather than black.

Conclusions

Given below are the important conclusions from this survey and from the analysis of work by other investigators. Because of the limited number of samples and sampling locations in the present survey, the numerical values in Table VI represent a combination of straightforward statistical weighting and judgment based on less tangible factors. It should be emphasized that to a certain extent, results are dependent on the analysis methods used.

Variation in Properties and Concentration

(1) The differences in particle character and concentration between clean non industrial cities such as Minneapolis and polluted industrial cities are much greater than the differences in size distribution.

(2) The variations in normal airborne dust are large enough to make it suitable as a test dust only for rough performance testing of air cleaners.

(3) For Minneapolis, summer dust is significantly finer, lighter colored, of lower concentration and less bimodal in size distribution than dust during the rest of the year. This may be attributed to a reduction in the carbonaceous and fly ash particles during the summer.

(4) The large differences in the amount of fibrous particles found in different locations may have very significant effects on the operation of air cleaners. This conclusion being substantiated by current research on filter life.

Miscellaneous Conclusions

(1) In normal airborne dust most staining is done by particles less than 5 μ in size.

(2) Most airborne dust aggregates are tightly bonded together and require severe mechanical dispersion to break them up.

(3) Natural airborne dust particles collected in bulk suffer irreversible agglomeration due to polymerization of compounds in the dust.

(4) The millipore filter sampling and sedimentation weight concentration and size analysis technique is convenient, rapid and flexible. It appears to be well suited to general purpose airborne dust evaluation.

TABLE VI

Properties of Average Airborne Dust

Property	Range	Average
*Weight geometric mean size — D_{g3}	0.8 -8	3μ
Number geometric mean size — D_{g1}	- to 0.2	0.03μ
Particle density	1.5 -3.0	2.1 gm./cc.
Porosity —	0.85-0.5	0.65
Bulk density	0.2 -1.5	0.7 gm./cc.
†Fraction fiberous particles	3 -35	10%
*Upper particle size	15 -50	25μ
Settling velocity	2 -10	3 cm./sec.
Dust fall	0.4 -10	1.5 O.D.D.
Size distributions	(See Fig. 3 & 5)	
Concentration	(See Fig. 7 & 9)	
Physical shape of particles	(See Fig. 9)	

*This is the Stoke's equivalent spherical size calculated from settling velocity. Large irregular particles of low density such as lint may be much larger physically in one or more dimensions.

†The values given here represent the actual fraction of particles that can be considered fibrous. This will be from 50 to 90% of the weight of dust that can be caught on the 170 mesh screens used on the millipore samplers.

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Fifty Years of Electrostatic Precipitation*

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Electrostatic precipitation has been closely identified with air pollution control ever since F. G. Cottrell succeeded in converting the phenomenon from a laboratory curiosity to a successful engineering process just 50 years ago. It is, therefore, particularly fitting on the occasion of the Golden Jubilee Meeting of the Air Pollution Control Association to recount the historical origins, growth, and significance of the process as a major element in the control of air pollution.

The parallel between the beginnings of the Air Pollution Control Association and the practical development of electrostatic precipitation during the first decade of the century is probably more than a coincidence. In a sense both were generated by the same social and technical forces. The renascence of science and technology during the waning years of the nineteenth century provided the tools, while the social pressures and reactions against the widespread damaging effects of air pollution provided the motivation for controlling smoke and dust emission from industrial plants.

These pressures were especially strong in the western states where smoldering conflicts between the farmers, re-enforced by the United States Forest Service, and the rapidly growing copper smelter industry frequently erupted into legal action against the smelters. Against this background, Cottrell, a native Californian schooled in physical chemistry in Germany under Ostwald and regarded as the most brilliant young mind in the rapidly rising Chemistry Department of the University of California, applied his talents and energies to the technical problem of collecting or precipitating the objectionable smoke and fume particles from stack gases.

Although the industrial smoke and dust problem was by no means new, existing control methods had proved to be impracticable or incapable of coping with the complexities of treating huge volumes of hot, dirty, and often corrosive gases. It was perhaps natural in these beginning years of the age of electricity to turn to electrical forces as a means of solving the smoke problem. Indeed, the electrical approach, based on Sir Oliver Lodge's work, had been tried unsuccessfully some 20 years earlier in England in an attempt to collect lead oxide fume.

Cottrell's success with the electrical method of cleaning gases is ascribable chiefly to his recognition of the need for a better method of supplying the high-voltage power essential for the process. For this purpose, he turned to the rapidly developing field of alternating-current electricity and adapted the high-voltage transformer and synchronous switch rectifier to his purpose. This approach, although obvious today, was remarkable at the time as an example of intuitive action toward an effective solution of a previously baffling problem.

A few words regarding the origins of the several identifying terms or names for the electrical process for separating particles from gases may be of interest. The term *electrostatic precipitation* used in the title of this paper is of quite recent origin and actually is less accurate than the earlier expression *electrical precipitation*. The process is not truly *electrostatic* since corona currents of some magnitude usually occur. Nevertheless, the present trend is to include all high-voltage, low-current phenomena in the field of electrostatics. The first use of *electrical precipitation* is uncertain. Dion, in a patent filed in 1904, speaks of *particles or masses already precipitated by the action of the electric current*. Cottrell in 1909 used the expression *the precipitating action of electrical charges*, while in a 1914 paper he used *electrical precipitation* freely. The term *Cottrell precipitator* apparently originated in the smelter industry where it was used as early as 1912.

The electrical process for separating particles from gases is unique in many respects. It is not limited by particle size as are gravitation and inertial methods. Nor is it limited by resistance to the motion of the gas as are ordinary filters and scrubbers. An analogy may be drawn to a filter or scrubber with streams of gas ions as the medium, a medium so imponderable that its resistance to gas flow is negligible. The separating forces are applied directly to the particles themselves instead of to the entire gas stream as in most mechanical methods. This direct and economical use of forces explains the modest power requirements and low draft loss of the electrical method.

There is no fundamental limit to cleaning efficiency attainable. In practice, it is seldom worth while to design precipitators for less than 80% efficiency, while most installations are in the range of 90 to 99%, with some up to 99.99%. The high collection efficiency, together with wide flexibility in gas flow capacity, gas temperature and pressure, type and amount of particulates collected, and ability to cope with corrosive atmospheres and particles, account for the wide application and acceptance of the method. On the other hand, precipitators generally do not compete economically with simpler collectors based on mechanical forces in those cases where the latter provide adequate performance, as, for example, in the collection of coarse dusts.

The work of Cottrell, aided particularly by the contributions of W. A. Schmidt, laid the foundations for the rapid and widespread application of electrostatic precipitation for controlling air pollution in the smelter and cement industries. Extension to other industries started early in the second decade of the century and continues to this day. Noteworthy expansion has occurred particularly since World War II and gives every promise of continuing at a high level.

* Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

The original application for air pollution control has remained the most important one, but of almost equal importance has been the recovery of valuable dusts and fumes for economic reasons. Other important applications include cleaning of fuel and chemical process gases, fractional collection of condensable vapors, and air conditioning of factories and offices.

The process is physical in character and perhaps is most accurately classified as electro-physics. Nevertheless, the actual practice of electrostatic precipitation involves a surprising number of scientific disciplines, including physics, chemistry, chemical engineering, electrical engineering, electronics, aero-dynamics, and civil engineering. Despite the physical nature of the process, it is interesting to note that much of the practical development beginning with the early work of Cottrell has been done by chemical and metallurgical engineers.

Historical Origins

The experimental fact that a piece of amber, on being rubbed, has the interesting property of attracting small bits and fibers was known to the Greeks, the discovery being attributed to Thales of Miletus, circa 600 B.C. The quantitative character of the electrostatic force involved was investigated by Coulomb and published during the period 1785 to 1789. Coulomb's discovery of the inverse square law forms the basis of the science of electrostatics and also is the starting point for the theory of electrostatic precipitation.

The first recorded reference to the electrical attraction of smoke particles appears in the famous work *De Magnete* of the English court physician, William Gilbert, in the year 1600. Gilbert describes the phenomenon thus, *Everything rushes towards electricks excepting flame and flaming bodies and the thinnest air . . . Yet they entice smoke sent out by an extinguished light . . . Bodies are borne towards electricks in a straight line towards the center of the electrick.* It is also of interest to note that in about 1745 Benjamin Franklin began the study of the effect of points *in drawing off and throwing off the electric fire.* Franklin's work seems to be the first on what we now refer to as the corona or brush discharge from sharp points. Experimental observations on electric discharges through smoke-

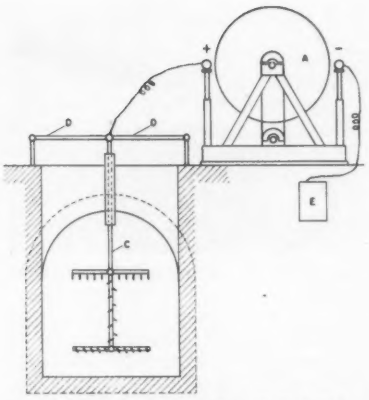

Fig. 1. Illustration from First United States Patent on Electrostatic Precipitation. A. O. Walker, No. 342,548 (1886).

filled gases and on the electric wind were also made by Beccaria in 1772.

Hohlfeld, in 1824, performed the experiment of clearing fog in a jar containing an electrified point, while Guitard repeated the experiment in 1850 using tobacco smoke in a glass cylinder described as being 9 in. in diam. and 18 in. long. However, Hohlfeld's and Guitard's experiments did not stimulate any practical study of the electrostatic precipitation principle and were soon forgotten. They were brought to light again by Sir Oliver Lodge in 1905, many years after he had independently rediscovered the same phenomenon and brought it to public attention in 1884. The work of two other experimenters appearing in the period between Guitard and Lodge also may be noted. Gaugain, in 1862, published what are probably the first experiments on the disruptive discharge between concentric cylinder electrodes. Nahrwold, in 1878, experimented with the discharge from a sewing needle point in a tin cylinder and noticed that the electric discharge greatly increased the rate of settling or collection of atmospheric dust. He also tried coating the walls of the cylinder with glycerine to make the collected particles adhere; this was probably the first recognition of the difficulty of retaining dry particles on the collecting surface.

The first attempt to apply electrical precipitation commercially was made by Walker and Hutchings at a lead smelting works in Bagillt, North Wales, in 1885 as the result of Sir Oliver Lodge's researches on the subject. A description of the installation, illustrated schematically in Fig. 1, was published by Hutchings as consisting of a system of metallic points situated in the flue from the lead furnaces, and excited from 2 Wimhurst influence machines with glass plates 5 ft. in diam., each machine being driven by a one-horsepower steam engine. The installation failed of its purpose, owing in part to the primitive method of producing high-tension electricity, and in part to the unfortunate choice of lead fume for the first commercial test. Lead fume is one of the most difficult dispersoids to precipitate because of its highly insulating character and very finely-divided state.

As is frequently the case in pioneer work, another investigator working independently rediscovered and patented electrostatic precipitation at about the same time. The investigator in this instance was Karl Moeller of Brackwede, Germany. The idea was apparently suggested to him by Nahrwold's paper. Moeller's patent, however, was issued a few months after Walker's first patent. A few other articles and patents appeared in the years following Lodge's work and Lodge himself took out another patent in 1903 covering the use of the then new mercury-arc rectifier for supplying high-voltage unidirectional currents for electrostatic precipitation. None of this work, however, was carried to the commercial stage, and electrostatic precipitation remained what it had been in 1885, a curious and intriguing laboratory experiment.

Cottrell's interest in gas cleaning seems to have originated not from the scientific aspect, but rather from the practical issue of controlling air pollution from smelters. Neither was his initial work in this field electrical, but instead was based on a more prosaic approach using the principle of the ordinary centrifuge. There is no clear-cut record as to the events which led Cottrell to the electrical method. However, we can be certain that he was dissatisfied with the gas centrifuge method. Furthermore, Cottrell was working in an era of great research activity on electrical discharges in gases and rapid development of high-voltage alternating-current technology.

Cottrell's first experimental work was on a small laboratory scale using a spark coil and a few discharge points in a chamber, an arrangement which worked quite well. (Fig. 4.) In attempting to increase the precipitation capacity by using more discharge points, Cottrell found that the corona or brush discharge would

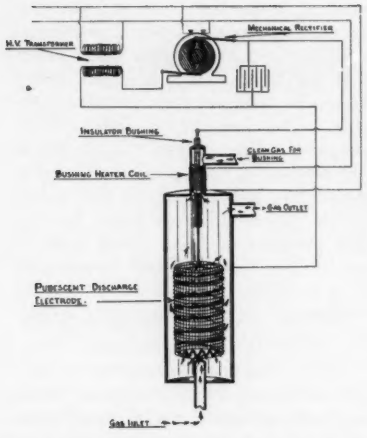

Fig. 2. Illustration from Cottrell's First Electrostatic Precipitation Patent. No. 895,729 (1908).

transfer from point to point, but would discharge from only 1 or 2 points at a time (because of insufficient power from the spark coil). To correct this, Cottrell, as a result of the partially-accidental discovery that a cotton-covered wire gave a continuous glow on its surface, devised the pubescent electrode made of semiconducting fibrous material which in effect provided many small discharge points. The pubescent electrode gave a fairly uniform corona over its whole surface, even at the low power provided by the spark coil, and functioned where the multiple discharge points failed.

Realizing the need for a better source of high potential electrical energy, Cottrell in 1906 turned to the newly-developed synchronous mechanical rectifier and high-voltage alternating-current transformer. (Fig. 3.) However, transformer voltages then readily attainable were limited to values of around 10 to 15 kv., and the pubescent electrode still proved an important adjunct in obtaining reasonably uniform corona over extended lengths of discharge electrode. The first experiments using the synchronous rectifier were made at the University of California in 1906 to precipitate sulfuric acid fume in a small test precipitator of a few cfm. capacity. The choice of sulfuric acid fume for the first experiment was a fortunate one for this material, although easy to collect by electrostatic precipitation, was frustratingly difficult by the mechanical and wet methods then available. The gratifying success of these experiments soon led to the installation of commercial

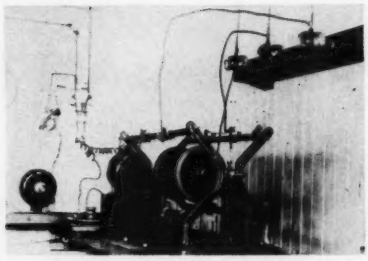

Fig. 3. One of Cottrell's Early Laboratory Rectifiers.

equipment, first at a powder works at Pinole, a few miles up the bay from Berkeley, and then at the nearby Selby smelter which was at that time embroiled in acute air pollution difficulties. These first commercial precipitators, although crude in construction, were sound in principle. The Selby unit operated satisfactorily for many years. It handled about 5000 cfm. of gas from parting kettles for precious metal recovery and collected about 2 gal./min. of sulfuric acid which previously had been discharged to the atmosphere in the form of a fine mist.

The essential features of Cottrell's precipitation system are shown in Fig. 2 which is reproduced from his first patent issued in 1908. Particularly to be noted are the synchronous rectifier and high-voltage step-up transformer, the pubescent discharge electrode, and the heater and ventilating system for keeping the high-voltage insulator clean and dry. Not indicated in the drawing, but of equal importance, was the use of negative corona which Cottrell showed to be superior to positive corona because of the much higher voltages and currents which could be carried with the negative discharge.

The success of the electric treater at Selby in the collection of previously intractable sulfuric acid mist provided strong impetus to apply the new process to larger problems in the smelter field. Cottrell's third commercial precipitator in the summer of 1910 was, therefore, not only on the much larger scale of 250,000 cfm., but also was applied to the more formidable problem of collecting lead and zinc oxide fume at the Balaklala smelter located in the Copper Crescent district of northern California. Despite his reasonably adequate electrical equipment and precipitator size, operation was far from smooth and had many baffling aspects. Nevertheless, these difficulties were gradually overcome and collection efficiency was brought up to around 80 to 90%, with recovery of about 3 tons of fume precipitate/day. It is of interest to note that the cost of this entire precipitation system including auxiliary flues, fans, and fume disposal means was approximately $110,000 or a little over 40 cents/cfm. Although the Balaklala smelter was finally shut down in July, 1911, on account of the sulfur dioxide nuisance which the precipitator could not of course correct, the installation did demonstrate the practicability of really large-scale electrostatic precipitation and soon led to the widespread adoption of the Cottrell process throughout the western smelter region.

Fig. 4. Cottrell's Experimental Precipitation Equipment for Collection of Sulfuric Acid Mist, University of California, 1906.

Air pollution problems during this period were by no means limited to smelters, and the next great advance in electrostatic precipitation came from an entirely different field, the Portland Cement industry in southern California. Lime and clay dust, emitted in large quantities from the cement kilns, settled on surrounding orange groves with damaging and costly effect. Cottrell, in answer to a query from the Riverside Portland Cement Company, believed that the precipitation process could be successfully applied to solve this difficult problem. New factors of size and complexity were involved in treating over 1,000,000 cfm. of gas carrying 100 tons of dust/day at gas temperatures of 400 to 500°C.

The task of devising and constructing practical electrostatic precipitation equipment to meet these conditions was undertaken in 1910 by W. A. Schmidt, a former student of Cottrell's at the University of California. During the course of this work, Schmidt introduced and patented what has since proved to be one of the most fundamental advances in precipitation technology — the fine wire corona-discharge electrode. This new concept overcame the limitations and practical difficulties inherent in the pubescent electrode and provided

the missing element essential for the large-scale development of the Cottrell process.

Schmidt's work at Riverside was also notable in other directions. Experimentation and exploration of the mysteries and intricacies of the new process were in order and were pursued with zeal. Investigations included collecting electrodes, methods of supplying high potential current, effects of sectionalizing the precipitator, and methods of controlling creepage and re-entrainment of collected dust. For example, experimental work was conducted on collecting pipes up to 4 ft. in diam., operated at potentials of over 100 kv. Many of the subsequent advances in the art of electrostatic precipitation may be traced to these pioneering investigations. Incidentally, the Riverside precipitator is still in operation at high efficiency and without structural changes.

With the successful completion of the Riverside installation in 1912 and the rapid application of the process throughout the smelter field, electrostatic precipitation passed from infancy to childhood and adolescence. It was also at this juncture that Cottrell, a man of extremely broad interests and idealistic nature, transferred his activities to other fields and except for a few published papers was never again active in electrical precipitation. With the financial backing of several associates, he had formed Western Precipitation Company in 1907 to handle the commercial phases of his electrostatic precipitation endeavor. Cottrell had long cherished the idea of establishing a non-profit foundation to administer and market patents emanating from universities and other similar institutions, with the net profits from such business to be used for the furtherance of scientific research. To this end in 1912, with the financial aid of a group of prominent industrialists and educators, he organized the Research Corporation and turned over to it his valuable precipitation patent rights for the United States east of the Rocky Mountains, with the exception of the cement industry, as an initial endowment. His remaining interest, which included patent rights for the western states for the cement field throughout the United States and world rights on all applications other than those assigned for the eastern United States were given to W. A. Schmidt.

Growth and Applications

Practical demonstrations of the utility of the electrical process for large-scale high-efficiency cleaning of furnace and process gases during the years 1907 to 1912 opened the way for the rapid growth and expansion of electrostatic precipitation which soon followed. Although the world-wide growth of the process is of interest, it is necessary for practical reasons to limit the present account to the United States. Developments in Europe, the most important area outside of this country, have largely paralleled those here, even though details of the technology and some of the applications differ.

The plan adopted in preparing this section is to divide the applications into major industrial fields or areas. This is necessary in order to maintain a logical and understandable approach as well as to define the important fields of application for electrostatic precipitation. Over-all summaries and data on the range of operating conditions and performance of precipitators are given at the end of this section.

Metallurgical Applications

Copper, lead, and zinc smelters

As would be expected, the Cottrell process was seized upon and developed very rapidly by the western smelters as a counter measure in their desperate legal struggle against fume damage suits. Other gas cleaning methods had proved inadequate or ineffective in solving these problems. For example, huge settling chambers in the form of extremely long and wide flues collected only dust particles, with most of the fine fume pouring out of the stacks. Filtration through woolen bags had been in use in lead smelting, but was scarcely applicable in copper smelting because the gases were much hotter and usually carried considerable sulfuric acid and both of these conditions caused rapid deterioration of the bags.

Although precipitator applications in the smelter field were made initially to abate the serious smoke nuisance, an even greater usefulness was soon found in recovering the valuable copper, lead, and zinc oxides and other compounds carried out of the stacks in the form of dust and fume from the furnace operations. In large installations the recovered particles which amounted to many tons ran to hundreds or even to thousands of dollars/day, and recovery was a matter of simple economics. Most of the western smelters, following their traditional philosophy of self-sufficiency, designed and built their own precipitators under patent license agreements. As a result, rather striking differences developed in their precipitation technology and practices as compared to the rest of the precipitation industry.

Experimental work on the electrical treatment of copper converter furnace gases was started as early as 1911 at the Garfield, Utah, smelter, while a year later the work was extended to a full-scale unit of 50000 cfm. capacity. The successful results obtained on converter gases encouraged the Garfield group early in 1913 to extend their experimental work to the treatment of gases from lead blast furnaces, MacDougall roasters, and reverberatory furnaces. High-efficiency performance was obtained on all of these gases separately as well as when mixed together.

Development of electrostatic precipitation at the giant Anaconda smelter also was begun during this period. Because of the very large volumes of gases to be treated, the use of 5 in. diam. collector pipes such as were used at Garfield would have been prohibitive in cost on account of the tremendous number of pipes required. For this reason the initial approach at Anaconda was in the direction of large pipes, 12 to 36 in. in diam. and 20 ft. long, (See Fig. 5, current off, and Fig. 6 current on,) powered by rectifier sets of 150,000 volts capacity. Somewhat later even larger pipes of 48 in. diam., operated from 220,000-v. rectifiers, were tested. However, these extremely large pipes proved to have their own disadvantages, chiefly the lengths of 20 ft. or more necessary for good efficiency and the very high voltages of 150,000 to 200,000 required to generate the corona. The full-scale Anaconda precipitator, therefore, was built with box- or plate-type collecting electrodes in a vertical flow arrangement for a treatment capacity of 700,000 cfm. This unit went into operation in 1916 and would classify as a large installation even by today's standards. Another early smelter installation which illustrates the line of development during that period was at Trail, British Columbia. This precipitator, built in 1914, was for a capacity of 100,000 cfm. and used collecting pipes 13 in. in diam.

Technology of the process was advanced and developed simultaneously with the applications. Perhaps the most important discovery of the period was the so-called conditioning of gases to render the particles conductive. This lack of conductivity of precipitated deposits undoubtedly was a major factor in the failure of Lodge's early work and also plagued Cottrell in his work at Balaklala. The discovery of conditioning, made during the Garfield experiments in 1912, was in a sense accidental. It was observed in the preliminary work on the converter gases that during periods when considerable sulfur trioxide was present, the coating on the pipes from the condensed fume was conductive and the process offered no difficulties; but that during periods of low sulfur trioxide, nonconductive deposits were formed in the pipes and after a short time the current was interrupted and further precipitation ceased. In addition to the conditioning effect of sulfur trioxide, it was found that conditioning by moisture, in the form of fine sprays injected into the gas, was very effective. Although in full commercial practice at Garfield, the fluctuation in sulfur trioxide content of the gases and the need for conditioning was circumvented by mixing the gases from several converter furnaces, the discovery of sulfur trioxide and moisture conditioning made possible the successful application of the process to many otherwise non-conductive or high-resistivity dusts and fumes, and provided the third essential element necessary for wide utilization of electrostatic precipitation.

Another valuable development at Garfield which was soon elaborated on at Anaconda was the principle of fractional precipitation. During the work on the converter gases, it was found that even practically complete removal of the lead fume and clarification of the gas at a temperature of 340°C. still resulted in a cloudy discharge from the stack. To obtain complete clearance of the stack it was necessary to cool the gases to 90°C. The explanation lay in the presence of arsenic trioxide and sulfur trioxide in the gas which were both in the vapor phase at 340°C., but condensed to fine fumes at 90°C. This finding suggested the possibility of effecting fractional condensation and separation of the fumes and vapors present by cooling the gases in several steps,

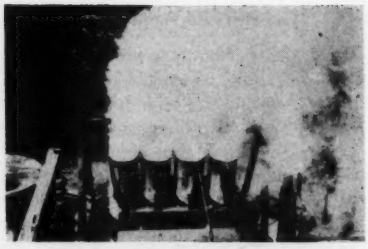

Fig. 5. Anaconda Leaching Plant Test Precipitator, Electric Power Off. C. 1913.

and using precipitation at each step to collect the component condensed at that temperature. The process was demonstrated shortly thereafter at Anaconda where refined, snow-white arsenic trioxide fume was separated and collected from the furnace gases.

Over the years precipitator applications in smelters have continued to increase. They are used extensively on copper, lead, and zinc reduction operations; copper roasters, converters, and reverberatory furnaces; Dwight-Lloyd sintering machines, blast furnaces, and reverberatory furnaces in lead; roasting of ore concentrates in zinc. Many of these are large installations.

However, the largest smelter precipitator in this country is undoubtedly the central gas-treating installation at Anaconda which was built and placed in operation in 1919. Gas flows of over 2,000,000 cfm. are handled in the treater. Gases from the precipitator are discharged through a monumental stack 585 ft. high and 60 ft. inside diam. at the base. The stack is an impressive sight and dominates Deer Lodge Valley from its location on a promontory 700 ft. above the smelter works and 1100 ft. above the valley. This precipitator, in addition to its size, is notable for the size and capacity of its rectifier equipment which comprises 12 full-wave mechanical rectifiers, each powered by a 100-kv., 75-kva. high-voltage

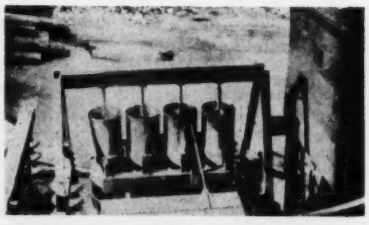

Fig. 6. Anaconda Leaching Plant Test Precipitator, Electric Power On. C. 1913.

transformer. A typical analysis of the precipitate shows on the order of 5% each of copper, zinc, and lead, and about 40% arsenic trioxide. Collection of the extremely fine arsenic trioxide fume by the Cottrell process provided the answer to the problem of arsenical poisoning of livestock in the surrounding agricultural region which originally had involved the smelter in severe damage suits.

Another important application of precipitators in the smelter area is in connection with the sulfur dioxide problem. Heavy emission of sulfur dioxide from sulfide ore roasting and other operations constitutes a serious potential source of damage to forests and vegetation over large areas adjacent to smelters. The Ducktown, Tennessee and Trail, British Columbia cases are among the best known examples of such damage.

Among the several successful methods for controlling sulfur dioxide emanations, that of conversion to sulfuric acid is the most important. The conversion may be effected either by the historic chamber process or by the modern contact or catalyst method. Both of these have been used in the smelter industry, but all of the later installations are based on the contact process. In this process the hot sulfurous furnace gases are first cooled to 300 or 400°F. and the entrained dust is removed in a dry precipitator. The cleaned gases are then passed through a scrubber for further cooling and then through an acid mist precipitator to remove acid formed from the sulfur trioxide naturally present in the furnace gases. After treatment in a coke-filled scrubber, the gases are passed through catalytic contact converter chambers for converting the sulfur dioxide to sulfur trioxide, and finally through absorption towers which turn out high-quality sulfuric acid. Although disposal of the large tonnages of acid produced originally was believed to be a major or impossible problem, the development of large markets for phosphate fertilizers not only solved the acid disposal problem, but also proved to be a profitable operation. Thus, the history of the smelter smoke problem, where correction of a serious and expensive air pollution situation actually turned out to be a profitable venture, was repeated.

Steel industry

This field although developed later than the non-ferrous smelter applica-

tions has long been an attractive one for electrostatic precipitators. The various operational functions in the steel industry where air pollution is a factor has resulted in numerous types of precipitator installations. In general, there are 2 classes of equipment used in this industry. The first type, such as used for the cleaning of blast furnace gas where the gas is cleaned for an economic purpose, and the second where air pollution problems are rampant, such as the cleaning of open hearth furnace gases, sintering machines, scarfing machines, Bessemer oxygen impingement processes, and electric furnaces.

The cleaning of blast furnace gas initially was studied before 1920. At this time, it was proposed to handle the gases on a hot, dry basis so that the sensible heat of the gases could be economically used. Troubles were encountered due to dust resistivity and fluctuating loads so that this application did not proceed very rapidly. It was not until about 1930, when the use of small checkers for better heat transfer in the hot stoves were introduced together with the development of the wet-film or water-flushed collecting electrode, that electrostatic precipitators came into their own in this field. This application has been a very important one and a large number of installations has been made. It is estimated that the gas capacity of the blast furnace precipitators installed in America totals about 15,000,000 ft.^{3} of gas/min. These precipitators have proved very satisfactory from an economic standpoint which is attested by their long life, low operating cost, and the exceptionally clean gas resulting from their operation.

An important application is the cleaning of open hearth furnace gases. This application is strictly one of removing suspended material for air pollution control purposes. The problem involves the cleaning of a gas from a cyclic process in which the volume, temperatures, dust content, and chemical content of the dust vary from hour to hour. The precipitators have operated very satisfactorily on this process. It is interesting to note that on one particular installation there was present an undesirable gaseous component which, for air pollution reasons, it was necessary to remove. This was done using a relatively old technique of adding a chemical to react with the gaseous component so that it could be fixed as a solid aerosol. In this particular case the precipitator operated not only on the native open hearth gas but on the reacted material as well. This field seems to be an ever-widening one for the air pollution pressures being exerted on the industry to clean these gases are very great, since the raw gas from an open hearth has the unhappy faculty of creating clouds of fume.

Another relatively recent application is the cleaning of gases from sintering machine operations. This application lends itself very well to precipitators. Precipitators have been used for the cleaning of gases from the machines using the hot scarfing processes. The cleaning of electric furnace gases has been done on a few installations and the records have indicated that the problem is not an easy one, although there is no reason why the successful use of a precipitator cannot be predicted. Another very interesting process is the use of precipitators for cleaning the gases from oxygen impingement steel processes. Equipment for this process is now being built. Extensive pilot plant work in both America and Europe has indicated that precipitators can do an excellent job in this field.

Precious metals

An interesting application which developed in the early 1920's was the recovery of gold from furnace and chemical operations at the United States Assay Office in New York City. This installation treated 70,000 cfm. of gas at an efficiency of over 95%. The gold recovered in fume deposits from the precipitator amounted to about $11,000/annum. Subsequently similar installations were made at several United States mints. Another application of some importance is the treatment of fumes from furnace operations for the production of metallic silver in connection with the electrolytic refining of copper.

Cement Industry

The cement industry is historically the second oldest application for the Cottrell process, dating from the pioneer work of W. A. Schmidt at Riverside, California in the years 1910 to 1912. It is also one of the largest in terms of number of installations and total gas treated. Precipitators are applied in several functional operations in this technology, including wet and dry process rotary clinkering kilns, shale and stone dryers, and grinding operations. This application, like that of fly ash, is hampered by the resistivity problem although it has been successfully circumvented in the latest designs. The information gleaned from the work on the resistivity of fly ash has played a very important role in the design of precipitators for this service. The gas cleaning installations for handling the situations created by the changes in the clinkering technology such as Lepold kilns and Fuller-Humboldt pre-heaters have been successfully designed. Like all applications where resistivity is a factor, the designer must be wary of designs that are not capable of handling high resistivity materials.

In the rotary kiln operation, which is the principal application for precipitators, waste gases are discharged at a temperature of from 400 to 600°F. for a wet process kiln and 1000 to 1600°F. for a dry process kiln, and carry suspended particles normally in the range of from 4 to 10 gr./ft.^{3} with some cases up to 20 to 40 gr./ft.^{3} Raw material comprising basically lime and clay minerals is charged to the kiln in the form of a finely ground powder carried either by air for dry process or by a water slurry for wet process. In general, the wet process kiln is easier to deal with from the standpoint of electrostatic precipitation chiefly because of the high moisture content and moderate temperature of the gas discharged from the kiln. In the case of dry process kilns, the gas temperature is reduced to the range of 600 to 700°F. ahead of the precipitator, usually by means of radiation cooling and air dilution, although spray cooling with water has been used to some extent in recent years. Dry plate-type precipitators are accepted practice in this field with most installations designed for 95 to 98% efficiency.

The general prospects for using large amounts of cement during the next 15 years augurs well for precipitators in this industry.

Chemical Industry

Electrostatic precipitators have been used by the chemical industry for a long time. Wherever a valuable aerosol is to be collected, where a gas is cleaned for subsequent use, or where atmospheric pollution must be controlled, precipitators have been used by chemical engineers. A com-

plete list of uses for this industry is beyond the scope of this paper. However, there are some very interesting applications which should be mentioned. Precipitators have been used in the sulfuric acid manufacturing industry since 1907. Cottrell's early experience at the Pinole, California, powder works attests their use in this field. In the manufacture of sulfuric acid by the contact process the gases, before entering the drying tower and after the scrubber, are generally treated in precipitators for the removal of acid mist. Inasmuch as small traces of acid mist are detrimental to the function of the catalyst extremely high efficiencies are necessary.

In chamber acid plants, particularly where metallic by-product gas is used, the gases are treated at elevated temperatures for dry dust removal before they enter the glover tower. As far as atmospheric pollution is concerned, in the sulfuric acid industry 2 important applications have been made, one for the cleaning of tail gas from the sulfuric acid contact processes and the other the tail gases from sulfuric acid concentrators.

In the chemical treatment of asphalt it is generally advisable to use precipitators on the blowing stills. Likewise the gases from gypsum kettles, dryers, and calciners can be treated very economically in the precipitators.

In the manufacture of phosphorus by the electric furnace method it is universal practice to treat the hot furnace gases to remove suspended dust before the elemental phosphorus is condensed. This results in a very pure phosphorus product in a very economical manner. Likewise, when phosphorus is oxidized and hydrated the phosphoric acid can be removed very conveniently with precipitators.

A relatively new application in the chemical field is the utilization of precipitators for the removal of tars from oil shale distillation gases. Here the precipitator does an excellent job in cleaning the gases which are subsequently condensed and treated to produce petro-chemical products.

Another application in the allied oil industry which played a large role in the war production of high octane gasoline is the use of precipitators for the recovery of catalyst in the cat cracker installations. A large number of precipitators are in use for this service and their use results in a reduction of catalyst lost from the system.

Detarring of Fuel Gases

The gasification of organic materials for the production of fuel gases results in the production of small amounts of tars which are carried by the gases. In order that the full economic value of the gases can be secured, these tars must be removed. Their removal, or detarring as it has been called, has proved one of the most popular and successful applications of electrostatic precipitators. In this general category, the detarring of water gas, coke oven gas, oil gas, and producer gas, are the striking examples.

The electrostatic removal of tars from these gases is a simple operation and a successful one. However, while this process may appear quite easy at the present time, it was not always readily acceptable by industry. Initially, there was a great deal of reluctance on the part of operators to accept a process in which sparking was inherent. There were a great many vague fears that the arcing would result in explosions of the fuel gas. Early pilot plant tests indicated that the explosion hazard was practically non-existent and after much study the method was accepted by the industry.

The precipitation of tars from these gases is technically straightforward inasmuch as the precipitated tars are free flowing and continuously steady conditions are secured. The broad acceptance of the method as an integral function in the gasification industry attests to the success of the process.

Beyond an occasional installation where corrosion occurs, the operating difficulties are practically non-existent. Installation costs, operating costs, and operating efficiencies secured are so favorable it is practically unthinkable for a design engineer not to include the equipment in gasification layouts.

Black Smoke

Collection of black smoke from the combustion of soft coal was one of the earliest applications considered for electrostatic precipitation, and also one having great popular appeal in an era of smoky cities caused largely by black plumes issuing from factory stacks and a myriad of home chimney pots. Cottrell, who must have found this subject wearisome, always maintained the fundamentally sound view that, with but few exceptions, the proper cure for the black smoke problem was not collection, but better and more efficient combustion to prevent its formation.

Some of the legitimate early cases where cleaning was justified included smoke emission from the manufacture of illuminating gas by pyrophoric decomposition of crude petroleum, smoke from locomotive roundhouses, and certain boiler plants where peak load conditions caused periodic emission of heavy black smoke. Precipitator installations for these purposes were made as early as 1912 in a western gas works and at the Bureau of Mines Fuel Experiment Station in Pittsburgh. Electrical collection of black smoke is not difficult aside from the problem of removing the light fluffy soot from the electrodes after deposit. In some cases, the soot proves sufficiently cohesive because of the presence of tars, while in other cases water sprays or wet films are necessary as a carrying vehicle for the sooty deposits.

Carbon Black

The application of precipitators to the economic collection of carbon black is a relatively old one. As early as 1920 precipitators were applied to small installations producing carbon black and lamp black for ink blending.

It was not, however, until the Second World War that this industry became a large user of electrostatic precipitators. The production of artificial rubber and its requirement for a type of carbon black which could be made in controlled gas volume furnaces was responsible for the large usage of precipitators in this field. While precipitators had been tried in pilot plant studies on gases from channel furnace buildings, the large volume of gas involved militated against their commercial usage because of high costs. The removal of carbon black from streams of furnace gases is generally done with an electrostatic precipitator followed by a mechanical collector. In this case, the precipitator acts as a size agglomerator to increase the efficiency of the mechanical collection. Most of the furnace plants use this system for the process collection of the black, however where air pollution problems arise a tertiary cleaning step is necessary — either bag filters or scrubbers — to provide the

clean stack gas necessary to allay pollution fears.

Paper Mills

The application of precipitators to the paper mill industry has been studied for a great many years. Actually an installation using precipitators for the recovery of salt cake from recovery furnace gases was made in Canada in the late teens. The impetus for the use of precipitators in this industry, however, did not materialize to any great extent until the 1930's when the manufacture of sulfate pulp from southern pine became a commercial possibility.

The initial applications in this field were dominated by the economic factors in the recovery of salt cake. The finding that a precipitator could operate on gases from an evaporator above the gas dewpoint led to its acceptance in the flowsheet of recovery furnace plants. The gases leaving the evaporators are at such temperature that dry precipitation could take place and the equipment could be built of steel since the corrosion was minimized. This application resulted in the collection of approximately 100 to 150 lb. of salt cake/ton of pulp which had previously been dispelled to the atmosphere. Practically all of the installations to date have been installed on the basis of the economic recovery of salt cake and since salt cake costs have risen very sharply during the last several years the economic attractiveness of precipitators has been enhanced. During the last 2 years consideration has been given to higher efficiency units in order that air pollution reduction can also be accomplished.

Electric Power Industry

The continued rapid increase in electric power consumption which on the average has doubled every decade since about 1900 has placed ever-increasing emphasis on fuel sources and power generation efficiency. Fossil fuels comprising coal, oil, and natural gas have been the most important energy sources for many years and by present indication will continue to be for at least several more decades. Hydroelectric power now accounts for only about 20% of the total, while the outlook for atomic power is a relatively slow long-term growth amounting to possibly 10 to 20% of the total by 1975.

Of the fossil fuels, coal is by far the most important for power production. Early power plants burned coal in stoker-fired boilers, but the drive for higher power generation efficiency led in 1919 to the successful development of pulverized coal as a basic fuel for the large highly efficient steam generating units characteristic of modern power plants. In this form of firing, the residual ash from the coal is entrained in the furnace gases in the form of finely divided particles commonly known as fly ash, and normally will be emitted from the stack unless special and effective means are provided for their removal. These minute fly ash particles may constitute ten percent or more of the coal burned and therefore may produce a serious air pollution problem.

Electrostatic precipitation was established early as the standard method for dealing with the fly ash problem; the first full-scale precipitator for this purpose was installed in Detroit, Michigan in 1923, only 4 years after the introduction of pulverized coal firing in power plants. Since then the use of precipitators for this purpose has paralleled the growth of the power industry and has for many years been the largest single field of application for electrostatic separators in this country. There are some steam power plants located in rural or remote areas which find mechanical fly ash collectors adequate for solving their air pollution problems, but these plants constitute only a small fraction of the total. The large majority of plants is located in cities or metropolitan areas and for these, electrostatic precipitators form an integral part of the boiler installations.

Development of the cyclone-fired furnace some 12 years ago in which the coal is burned in a coarse crushed form rather than in a pulverized state was at one time believed to provide a solution for the air pollution problem by eliminating the fly ash at the source. However, experience has only partly confirmed this expectation. It has been found that such boilers emit appreciable quantities of fine fume particles to the extent of about 20% by weight of the ash present in the coal. The considerable quantity and high visibility of this fume has necessitated installation of electrostatic precipitators to eliminate the nuisance.

The magnitude of the fly ash problem is strikingly shown by figures on the pulverized coal burned by the power utilities, which in 1948 amounted to some 65 million tons and by 1955 had risen to 140 million tons. Nor is there any indication of a slackening or reversal of this rate of increase in coming years. For example, studies recently made on energy sources for power production led to a projected figure of 440 million tons of coal/annum by steam power plants by 1980. This prediction takes into account the impact of atomic energy and all other foreseeable factors.

In addition to the sheer magnitude of the coal burned, the fly ash collection problem is constantly becoming more complex because of the rapid growth in boiler sizes, the general worsening of coal quality in the form of higher ash content and more variable ash characteristics, and the requirement for higher collection efficiencies and cleaner stacks. Maximum boiler capacities have about doubled in the past decade. The largest boilers in 1947 were rated at about one million lb. of steam/hr. whereas the present figure is two to two and one-half million lb./hr., with units up to three million lb./hr. being projected for installation in the next 2 or 3 years. In terms of flue gas to be cleaned, these figures correspond to about 0.5 million cfm. for a large boiler of 10 years ago, about one million cfm. for the largest boilers now in operation and, 1½ to possibly 2 million cfm. for the largest boilers now projected or being considered for installation within the next 2 or 3 years.

Collection efficiency requirements have also risen markedly over the years. The earliest fly ash precipitators of the 1920's were designed for 90% cleaning efficiency. By 1940 the standard had risen to around 95% and to about 97% by 1950. Requirements have now increased to 98 to 99% for precipitators in critical air pollution areas. The ultimate requirement for collector efficiency in the fly ash field is probably now being reached. A visually clear stack discharge, as determined both by fundamental optical considerations and by actual observations on existing power plant stacks, is obtained when the ash concentration is reduced to about 0.02 gr./ft.^{3} of gas. For most plants the fly ash concentration ahead of the collector is in the range of 2 to 4 gr./ft.^{3} which means a collector efficiency of 99 to 99.5% to achieve the ideal clean stack condition.

Marked changes have also occurred during the past 10 years or so in the interpretation and meaning of collector efficiency. These have arisen from the general practice of base loading the newer and more efficient generating units as well as the more stringent air pollution regulations of many cities. In earlier years, boilers were commonly operated at low load at night, and precipitators were heavily rapped at these low load periods when there would be little loss of ash from the stack. Efficiency tests made at full load during the day under these conditions did not fully reflect the losses caused by rapping the precipitator. By contrast, present day practice on new installations requires that the collector operate continuously day and night at or near full load and with continuous rapping to eliminate the old unsightly rapping puffs which are characteristic of intermittent rapping methods. It is clear that precipitator efficiency under modern stringent conditions has a meaning quite different than in earlier years and that basically improved precipitator designs are necessary to adequately meet these more rigid performance requirements.

While this application is the largest for electrostatic precipitation, it is probably also the most difficult one. Inherently the difficulty arises from the fact that at the time the boiler installation is planned there is at best only limited information available on the character of the ash to be experienced. This pertains not only to the particle size of the ash but also the resistivity which plays such an important role in the precipitation of this type of suspended material. While a large number of studies has been made to determine what may be expected from the burning of certain types of coals, other factors such as the operation of the boiler also influence ash characteristics, so that the designer must base his approach on statistical methods and experience with coals of similar nature. This method has proved to be moderately successful, however studies on this are continuing. It is very important that this phase of fly ash precipitation be established so that precipitator designs can be clarified.

Air Cleaning

Cleaning of factory ventilating air on a substantial scale of 55,000 ft.^{3}/min. was accomplished at a New Haven, Connecticut, arms plant in 1915. It should be noted, however, that no attempt was made to re-circulate the air. Recirculation of electrostatically-cleaned air in a ventilation system seems to have been first tried at an office building in Fresno, California, in 1923. One of the objects was to determine whether the ozone produced by the corona discharge in the precipitator would have any agreeable or beneficial effects on the office workers. Needless to say, the results were negative; but this was a period when ozonizers were popular.

General use of air cleaning precipitators did not start until the late 1930's with the introduction of the low-ozone type precipitator. The development of suitable precipitator equipment for air cleaning actually involved several problems. Industrial precipitators of the Cottrell type generate appreciable amounts of ozone when treating ordinary air. The ozone is produced in the visible corona glow sheaths which encompass the high-tension wires and may amount to several ppm. concentration by volume in the discharge air. This is far above permissible ozone levels which at present are established at 0.1 ppm. for factories and workshops and considerably less for home and office environments where longer exposures are probable.

In addition to the ozone problem, sharp reductions in size, operating voltages and cost were essential to the development of practical equipment for electronic air cleaning. Credit for achieving a satisfactory solution of these problems and developing practical equipment is principally due to the work of Penney in the middle 1930's. He utilized the 2-stage precipitator principle, conceived and patented some 20 years earlier by Schmidt, for his basic design. Reduction of ozone generation in the particle charging stage was accomplished by using very fine tungsten wires of 5 to 10 mils diam. operated at relatively low voltages and currents of positive polarity. Compact size and lowered cost of the particle collecting section were achieved by using light aluminum plates spaced about ¼ inch apart. These basic design features were incorporated in the original Precipitron first marketed by Westinghouse in the late 1930's and copied widely since then by other groups selling electrostatic air cleaning equipment.

Electrostatic air cleaning has come into rather general use in many manufacturing and process operations where dust-free air is essential as, for example, in the manufacture of photographic emulsions, assembly of optical instruments, fabric and spinning operations, and cleaning blower air for blast furnaces in steel mills. It is also used in many office buildings and commercial establish-

TABLE I

Pioneer Precipitator Installations 1907-1920

No.	Application	Date	Location
1	Sulfuric acid mist from contact acid plant, 200 cfm.	1907	Pinole, Calif.
2	Smelter, zinc and lead fumes, 300,000 cfm.	1910	Shasta Co., Cal. Balaklala
3	Cement kiln dust, 1,000,000 cfm.	1912	Riverside, Cal.
4	Copper converter (lead fume), 200,000 cfm.	1912	Garfield, Utah Amer. Smelting and Refining Co.
5	Gold and silver recovery from furnace treatment of electrolytic copper slimes.	1913	Perth Amboy, N. J. Raritan Copper Works
6	Absorption of chlorine gas by powdered lime followed by precipitator collection	1913	Niagara Falls, New York. Hooker Electro-Chemical
7	Dwight-Lloyd sintering machine lead fume. 20,000 cfm.	1914	Tooele, Utah Inter. Smelting and Refining Co.
8	Tar removal from illuminating gas; 25,000 cfm.	1915	Portland, Oregon
9	Cleaning ventilating air in factory; air not recirculated 55,000 cfm.	1915	New Haven, Conn. Winchester Arms
10	Paper-pulp recovery of alkali salts from waste liquor evap. gases; 90,000 cfm.	1916	Canada
11	Central gas cleaning plant; 2,000,000 cfm.	1919	Anaconda, Mont. Anaconda Copper Smelting Co.

TABLE II

Summary of United States Precipitator Installations in Major Fields of Application, 1907-1957

(See Fig. 7.)

Application	1st install.	No. pptrs.	Gas flow million cfm.	
Electrical Power Industry: (Fly Ash)	1923	730		157
Metallurgical:				43.4
Copper, lead and zinc	1910	200	15	
Steel industry	1919	312	22.5	
Aluminum smelters	1949	88	5.9	
Cement Industry:	1911	215		29
Paper Mills:	1916	160		18.0
Chemical Industry:	1907	500		9
Detarring of Fuel Gases:	1915	600		4.5
Carbon Black:	1926	50		3.3
Total:		2855		264.2

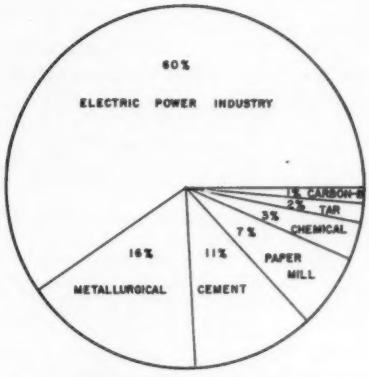

Fig. 7. Relative Distribution of Precipitators in Major Fields of Application on the Basis of Installed CFM Capacity.

ments, as well as to a limited degree in homes, particularly by persons sensitive to certain types of air-borne allergens.

Summary of Precipitator Installations and Operating Conditions

Estimates of the world-wide application of precipitators are very difficult and probably impossible to make at the present time. However, it is possible to make reasonably good estimates of the major applications of precipitators in the United States and a summary of these is given in Table II. It is believed that the figures included in the table are reasonably accurate and representative. All of the major applications are included and probably would account for at least 90% of the total if all of the various miscellaneous applications were also included. The least reliable figure in the table is that for copper, lead, and zinc metallurgical applications as it has been necessary to make fairly rough approximations. The figures for the electric power industry are believed to be accurate within about 5%. It will be noted that this latter industry accounts for 60% of the total on an installed cfm. basis as indicated in the diagram, Fig. 7.

Table III is a summary of the range of operating conditions for precipitators actually installed. These figures do not necessarily correspond to the theoretical limitations as will be clear from the context of the table.

Summaries of Published Papers, United States Patents, and Landmarks

Literature — Scientific and Technical Papers

The published literature on electrostatic precipitation is extensive and scattered in many fields of application. Practically all of the American scientific and technical societies have published articles on the subject, while the same situation exists in European publications. A reasonably complete bibliography of published papers, including both American and foreign, prepared in 1945 showed between 500 and 600 total. Recent estimates show a great increase during the past 10 years and the present figure may be taken as approximately 1000 total published papers in the field. An annotated list of major historical and technical interest is included in the bibliography.

United States Patents: Electrostatic Precipitation, 1886-1957

There is a large number of patents in the field of electrostatic precipitation, both in the United States and in foreign countries, particularly Great Britain and Germany. Many of the patents in different countries are overlapping so that the United States patents may be taken as representative of the entire field and these may be broken down into the following major categories.

Collecting and discharge electrodes	100
Electrode cleaning means	50
Precipitator applications	150
Two-stage precipitators	100
Combination precipitators (electro-mechanical, electro-scrubber, etc.)	100
Electrical energization	50
Details of construction	200
Miscellaneous	~250
TOTAL for the period 1886-1957	~1000

A selected list of patents is shown in Table IV.

Horizons

The general outlook for electrostatic precipitation is one of expanding growth in both old and new ap-

TABLE III

Range of Precipitator Operating Conditions

Gas flow	1 to over 2,000,000 cfm.
Gas temperature	to 1200°F.
Gas pressure	to 150 psi.
Gas velocity	3 to 15 ft./sec. for most applications; 25 to 50 ft./sec. for a few special air cleaning units
Draft loss	0.1 to 0.5 in. w.g.
Particle size	0.1 to 200+ μ
Particle concentration	0.0001 to 100 gr./ft.^{3}
Particle composition	no basic limit; solid, liquid, corrosive chemicals
Treatment time	1 to 10 sec. for most applications; as low as 0.1 for a few special cases
Efficiency	most applications 80 to 99%; some 99.9+%

TABLE IV

Selected List of Basic United States Patents on Electrostatic Precipitation

1886	First patent on electrostatic precipitation. A. O. Walker, No. 342,548.
1899	Combination precipitator and scrubber. B. H. Thwaite, No. 617,618.
1904	Synchronous mechanical rectifier. H. Lemp, No. 774,090.
1905	Mercury vapor rectifier tube for electrostatic precipitators. O. J. Lodge, No. 803,180.
1908	Combination cyclone and electrostatic precipitator. L. N. Morscher, No. 888,638.
1908	Cottrell's first precipitation patent; use of rectified alternating current. F. G. Cottrell, No. 895,729.
1913	Use of negative polarity. F. G. Cottrell, No. 1,067,974.
1915	Shielded screen pocket collecting electrode. W. A. Schmidt, and G. C. Roberts, No. 1,132,124.
1916	Fractional precipitation by successive condensation. W. A. Schmidt and L. Bradley, No. 1,204,906.
1917	Removal of contaminant gases by electrostatic precipitation. L. Bradley and W. A. Schmidt, No. 1,221,505.
1917	Liquid-film precipitator. H. A. Burns, No. 1,250,088.
1919	Combination of mechanical and electrostatic collection. W. A. Schmidt, No. 1,298,409.
1920	Conditioning and cooling gases by water spray ahead of precipitator. E. R. Wolcott, No. 1,329,737.
1920	Fine wire corona electrode and two-stage precipitation system. W. A. Schmidt, No. 1,343,285.
1935	Half-wave energization of precipitators. H. A. Wintermute, No. 2,000,654.
1938	Low-ozone air cleaning precipitator. G. W. Penney, No. 2,129,783.
1941	Automatic rectifier control. C. C. Levy, No. 1,976,569. H. E. Corbitt, No. 2,247,361. H. J. Hall, No. 2,742,104.
1942	Conservation of heat and temperature in vertical flow precipitator (paper mill). C. W. Hedberg, No. 2,297,555.
1950	Pulse energization of precipitators. H. J. White, No. 2,509,548.
1952	Continuous bank rapping of collecting electrodes. H. L. Richardson, No. 2,595,204.
1954	Wet Bottom paper mill precipitator, L. M. Roberts, A. N. Crowder, and S. Rabkin, No. 2,689,019.

plications. This expectation is based on the proved fundamental advantages and effectiveness of the method in meeting the diverse gas cleaning needs of modern industrial operations and processes. Of the 4 major areas of gas cleaning in which electrostatic collection is widely used, that of air pollution control probably will continue to be of first importance, while recovery of valuable particles from industrial furnace and process gases undoubtedly will remain a strong second. Beneficiation of chemical and fuel gases by electro-filtration has long been essential in many industries for economic reasons and may well be even more extensively used in the future. The use of electronic air cleaning for commercial air conditioning and for providing highly cleaned air for industrial purposes is growing rapidly.

Greatest growth in existing applications during the next decade may be expected in the electric power industry where the geometric increase in power consumption, the rapid rise of coal as the basic energy source for power generation, and the greater emphasis on air pollution control in American cities, combine to create an ever-increasing need for effective air pollution control equipment. Entirely new applications for the method undoubtedly will continue to develop with advancing technology in such fields as chemical, mineral, and other process industries. For example, the reduction and processing of new industrial metals as well as the development of newer methods for economically treating low-grade ores of classical metals will, in many cases, include large-scale gas cleaning as an integral part of the operations. The role of the process in the field of atomic energy is not yet clear. Up to the present, applications in this field have been peripheral and casual. However, more serious applications are likely to develop when the peacetime role and the economics of nuclear energy for civilian use become better crystallized.

Technology of electrostatic precipitation has developed rapidly since World War II, and activity in this area promises to continue at a high rate. Further advances may be expected in the next few years, particularly in the directions of *(1)* substantial reductions in precipitator size through fundamental improvements in electrode systems, gas flow, and methods of supplying electrical energy, *(2)* automatic rectifier control systems to insure optimum precipitator performance under fluctuating load and operating conditions, *(3)* rapid adoption of the new silicon rectifiers which appear almost ideal for supplying high-voltage rectified power to precipitators, and *(4)*

TABLE V

Scientific and Technological Landmarks

1824	First laboratory demonstration of the phenomenon of electrical precipitation. Hohlfeld.
1885	First attempt to apply electrostatic precipitation on a commercial scale. Walker, Hutchings, and Lodge.
1906	Introduction of high-voltage rectified alternating-current for supplying electrical energy to precipitator. Cottrell.
1907	First successful commercial precipitator. Applied process to high-efficiency collection of sulfuric acid mist. About 200 cfm. treated. Cottrell.
1912	Introduction of fine wire corona electrode. W. A. Schmidt.
1912	Concept and invention of two-stage precipitation system. W. A. Schmidt.
1912	Conditioning of gases by moisture and SO_3 to render particles conductive. W. H. Howard.
1913	Fractional electrostatic precipitation. Anaconda Copper Company, Anaconda, Montana.
1913	Application of precipitation to removal of contaminant gases (absorption of chlorine gas by powdered lime followed by collection of lime in precipitator). Hooker Electro-Chemical Company, Niagara Falls, New York.
1919	Experimental discovery of exponential law of electrostatic precipitation. E. Anderson.
1919	First application of electronic high-vacuum rectifier tubes to precipitation. S. Dushman.
1922	Theoretical derivation of exponential equation. Deutsch.
1923	First basic studies on electric charging of suspended particles in the corona field. H. Rohmann.
1932	Introduction of double half-wave rectifier circuit. Wintermute.
1935	Development of low-ozone air-cleaning precipitator. Penney.
1948	Development of continuous rapping.
1945	Introduction of high-voltage selenium rectifiers and silicon rectifiers for electrostatic precipitation.
1956	

development of better methods and equipment for collecting high-resistivity particles. Other major advances in precipitation technology may be foreseen in the complete automation of gas-cleaning and particle-handling equipment, replacement of present hopper methods by fundamentally better means for removing collected particles from precipitators, and development of faster and cheaper methods for determining performance of gas cleaning equipment.

Finally, progress is being made in correcting the somewhat chaotic condition which has resulted from the lack of accepted technical standards in the entire gas-cleaning industry, a situation which has often caused confusion and sometimes reduced the subject to an exercise in semantics. Although awareness of this problem was evinced in 1941 with the formulation by the American Society of Mechanical Engineers of power test codes which included standard methods for determining performance of gas cleaning equipment, general recognition and action by other groups has occurred only within the past few years. Work on standards for specifying and rating electrostatic precipitation equipment for fly ash, as well as on standard methods for determining the resistivity and chemical analysis of the many kinds of fly ash encountered in practice, are nearing completion in the Air Pollution Control Association. Badly needed standards for determining and specifying particle size in connection with mechanical collectors are also being worked on. Standards for high-voltage rectifier equipment for electrostatic precipitation are in the final stages of development in the American Institute of Electrical Engineers. Development and acceptance of these various standards should go far toward placing the entire field on a sounder basis and should materially aid users in the intelligent appraisal of the design and performance of electrostatic precipitation equipment.

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Methods of Combatting Air Pollution in Ferrous and Non-Ferrous Foundries*

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For more than 20 years the foundries of the United States have taken a leading role in the elimination of unhealthful dusts and fumes from the working areas within industrial plants. By the efforts to remove internal dust and fumes through the use of exhaust ventilation and dust-collecting systems, the castings industry became one of the foremost users of industrial dust-collection equipment. During this same period the foundry industry in conjunction with the dust-control equipment industry, built up an excellent background of knowledge and experience in the techniques of effective dust and fume control within its plants.

In fact, there is no other industry which has more universally adopted dust collectors of one type or another than has the foundry industry. Instances where dust-bearing ventilation air is discharged to atmosphere without cleaning are very rare. The problem is merely one of selecting a suitable dust arrester and no particular problems arise in connection with the prevention of air pollution from sources of this nature.

Thus shakeout, cleaning room and pattern-making operations have already been controlled in the foundry industry, but melting operations have presented an entirely new set of problems because of heat and corrosive gases.

As a basic step in air pollution control of hot emissions, the foundry industry has adopted operational changes as follows:

1. Control of melting time in order to obtain a uniform melting rate. This may be accomplished by:
   (a) The installation of a larger size holding ladle, thereby reducing melting rate fluctuation.
   (b) The use of blast-air controllers in order to maintain a uniform flow of combustion air through the charge thus reducing peaks or gusts of emissions discharged to atmosphere.
   (c) Keeping the charge depth at a maximum for the purpose of holding down the stack gas velocity and thus enabling the top part of the charge to act as a dust and cinder collector. This may aggravate the oil fume problem if adequate ignition temperature and combustion space are not available in the stack.
2. Proper handling of cupola coke in order to reduce the amount of coke particles carried out of the cupola stack. This may require:
   (a) Screening or forking of the coke before it is placed in the charging bucket.
   (b) Altering the method of adding coke to the charging bucket in order to reduce the distance the coke falls. Where coke and metal are added to the same bucket, the coke should always be added last.
   (c) Keeping the cupola as full as possible in order to keep coke from breaking during charging.
3. Briquetting of metal turnings before charging. This reduces the amount of coarse material emitted.
4. Using cleaned, well screened, unweathered limestone to minimize limestone dust in the emissions.
5. Removing, by means of a sprue mill, all possible sand from sprues and risers returned to the cupola for remelt.
6. Installing afterburners at the cupola charging door in order to maintain stack gas ignition at all times. Without afterburners, the cupola stack flame will oftentimes be extinguished when a charge is dropped into the cupola. These burners are installed above or opposite the charging door and completely consume combustible fines and oil vapors before discharge to atmosphere.
7. Increasing the stack height at least 25 ft. above the charging door in order to provide sufficient combustion time.
8. Avoiding the use of oil or grease-coated scrap, or using degreasing equipment.
9. Using gas burners or electric igniters during light-up time. The cupola bottom can be heated to much nearer the desired melting temperature and there will be less arching of the coke bed than would be the case if wood were used for ignition.
10. Adding lead pigs to the ladle rather than charging into the cupola when melting bronze alloys.

Control Equipment for Cupolas

In addition to these basic operational changes, foundrymen are adopting collection equipment of various degrees of efficiency according to local requirements. Some of these are as follows.

Simple Spray Washer

A simple spray washer consists of a cylindrical steel shell having a cross-sectional area at least twice that of the cupola stack, and mounted at the top of the cupola with a nonclogging

* Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

water-spray nozzle located just below the top of the shell, as shown in Fig. 1. Greater efficiency can be obtained by installing two spray nozzles, one below the other.

A drain pan mounted below the cylindrical collector shell collects the washer spray water and the entrained dust for return to the settling tank, normally located at ground level. The flow of hot gases through the collector shell puts cooling air through the opening between the drain pan and the collector shell.

The successful design of one cupola installation may produce disappointing performance on another cupola having the same outward size and characteristics, dué to the many variables in cupola gas conditions and the wide range of solids emitted.

Improved Cupola Gas Washer With Cone

For more effective air-pollution control, and at moderate increase in cost, the improved washer type may be installed. This improved wet cupola-gas washer is equipped with a steel cone over which the water is discharged in a spray or curtain, as shown in Fig. 2. The area between the cone and the shell should be 2 to 4 times the area of the cupola stack so as to allow the passage of dust-bearing gases at reduced velocity through a curtain of water spray. This permits the water to contact the exhaust gas, making it possible to wash out and collect practically all the coarse and part of the fine particulate matter. While the opacity of the stack discharge is not reduced to any great extent, a greater degree of collection efficiency has been obtained.

A circular ring baffle or deflecting ring (Fig. 3) inside the top of the collector shell removes water droplets and entrained solids. Within limits, the more water used in this type washer, the greater the efficiency.

With correct operational procedures and safeguards, such as interlocks between the water supply and the blower, maintenance costs on this type of equipment should be quite reasonable.

Design of this type collector makes it extremely difficult to conduct necessary tests to determine the effectiveness of the collector in accordance with accepted procedure. The wide discharge opening permits the gases to be emitted at velocities as low as 200 to 300 fpm., with no positive direction.

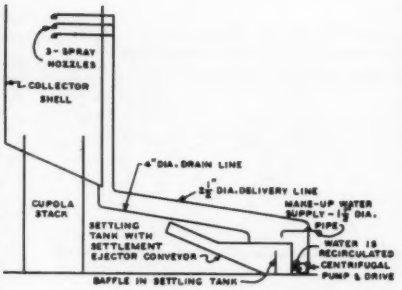

Fig. 1. Schematic diagram of simple spray washer for cupola dust collector and auxiliary equipment.

One series of tests on 2 improved cupola-gas washers is shown in Table I. Screen analysis of collected solids indicated good collection of large (above 44 μ) material.

The manufacturer of this equipment guarantees to remove down to 0.7 lbs./1000 lbs. of gases. If an adapter is used as shown in Fig. 4, the wet cap can be connected to a wet collector. With such a system, the manufacturer guarantees to remove down to 0.3 lbs./1000 lbs. of gases provided the cupola is operated under conventional conditions as described in the AFS handbook *The Cupola and Its Operation*.

The advantage of the arrangement is that the investment in the simpler equipment is retained if the code under which a plant operates becomes more severe.

Dry Mechanical or Centrifugal Collectors

Dry mechanical or centrifugal collectors provide a degree of control from cupola gases comparable to boiler fly-ash installations. Depending on design and pressure drop, removal efficiencies can be high in the dust fractions as low as the 5 to 10 μ range.

Installations, like other high efficiency collection systems, require capping of cupola, cooling the hot gases, installation of induced draft fan, and control system to open caps in case of system or utility failure.

Advantages include effective collection of particles in the *public nuisance* range; dry removal of solids which eliminates corrosion problems; adaptability to future fume and smoke removal by addition of a final cleaner of fabric or electrostatic designs.

High Efficiency Centrifugal

The high efficiency dry multiple centrifugal collector (Fig. 5) has recently been developed for application

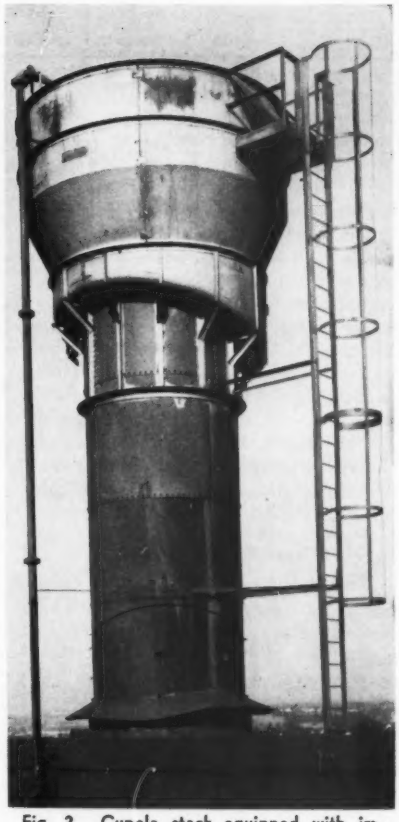

Fig. 2. Cupola stack equipped with improved cone-type gas washer.

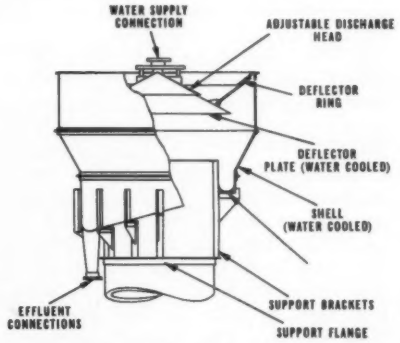

Fig. 3. Diagrammatic sketch of improved gas washer shown in Fig. 2.

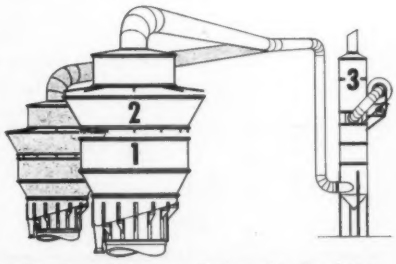

Fig. 4. Adapter on stack washer for future connection to wet collector.

TABLE I

Test Data for Emission From Two Improved Cupola-Gas Washers

Test No.	Dust emission rate, lb./hr.	Dust Concentrations in Effluent Gases: Gr./ft.³ @ 70°F.	Lb. dust/ 1000 lb. gas	Lb. dust/ ton of metal melted
1	84	0.40	0.76	8.0
2	60	0.31	0.58	6.6
3	59	0.30	0.57	5.9
4	88	0.40	0.76	10.3
5	88	0.40	0.76	10.3

to cupolas. There are several such installations in the Midwest. Performance data on full scale cupola installations indicate removal of cinder and dust particles that would otherwise settle on the foundry roof and neighborhood, and the reduction of concentration in effluent gases to values below those normally specified for boiler stack gases.

Fabric Filters Collectors

Where air pollution control ordinances are very stringent; or where foundry management has wanted to make provision now for a future stricter revision of an existing law; or where management has anticipated the future adoption of the strictest type of ordinance when no law of any kind is presently in effect, the fabric tube dust collector has been installed on many foundry cupolas. Fig. 6 shows a schematic diagram of an Orlon tube collector on a typical cupola installation.

Table III shows the performance data of this system installed on a 78-in. diam. cupola, lined to 54 in.

Electrostatic Precipitators

Electrostatic precipitators have been used successfully on both ferrous and non-ferrous cupolas but insofar as I know have not received wide acceptance principally because of cost. Efficiency is admittedly high. It has been used on both cold blast and hot blast cupolas. Fig. 7 shows an electrostatic precipitator connected to a cold blast cupola.

Fig. 8 shows an electrostatic precipitator connected to a hot blast cupola. It has been claimed that a hot blast system will pay for itself in a reasonable length of time because of the savings in fuel and increase in production.

Other Types of Equipment

Foundrymen have also installed on cupolas slotted cone-type and vortex collectors. The venturi scrubber has now been developed for cupola applications.

In general, foundrymen are selecting equipment types either on the basis of compelling ordinances or of anticipated ordinances. Many foundries have installed equipment in the interest of better community relations.

Control Equipment for Furnaces

Open-hearth furnaces are gradually being supplanted by electric arc furnaces in the foundry industry. Rather than spend money on collection equipment for open-hearth furnaces some managements prefer to change to electric furnaces which require less expensive control equipment and generate less fume because oxidation is less.

In the non-ferrous foundry industry, where crucible, barrel and kettle type furnaces and the like are used, little progress has been made in collection of emissions because of prohibitive costs.

For example, in many non-ferrous shops a large number of small furnaces is used. Because of the differ-

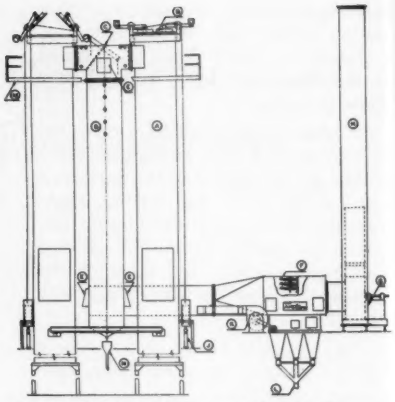

Fig. 5. High efficiency centrifugal collector installed on cupola.

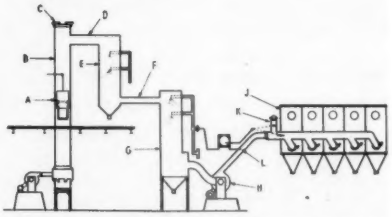

Fig. 6. Flow sketch of continuous automatic cupola fume collection system.

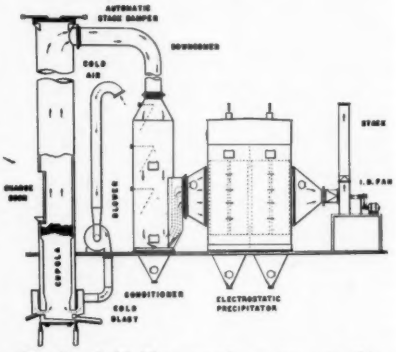

Fig. 7. Cold blast cupola system. In this arrangement, gases originating in the cupola pass through downcomer to conditioner, then to electrostatic precipitator, fan, stack and atmosphere.

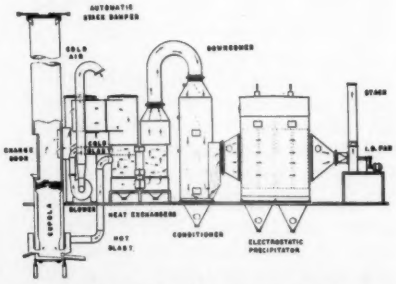

Fig. 8. Hot blast cupola system. In this arrangement, gases leave the cupola, pass first through the heat exchanger, then via downcomer to conditioner, to electrostatic precipitator, fan, stack and atmosphere.

TABLE II

Performance Data for High Efficiency Dry Centrifugal Cupola System (Average of 9 Tests)

Dust Loadings				Exit Concentration	
Inlet		Outlet			
Gr./scf.	Lbs./hr.	Gr./scf.	Lbs./hr.	Gr./ft.³ @ 500°F.	Lbs./1000 lbs. gas
0.94	267	0.22	63.0	0.12	0.42

NOTE: Compare exit concentrations to usual ASME acceptable loadings for boiler gases of 0.257 gr./ft.³ @ 500°F. or 0.35 lbs./1000 lbs. gas. Compare with revised Allegheny, Pa. Code for permissible cupola emissions of 0.50/1000 lb. gas.

TABLE III
Performance Data of a Fabric Tube Collector Installed on a 54in. I.D. Cupola

Ave. Vol. stack gases (cfm.)	29,000
Ave. stack temp. — °F.	1,580
Ave. Vol. stack gases @ 60°F. (cfm.)	7,400
Dust concentration in cupola stack gr./scf.	1.42
Process weight — lb./hr.	15,800
Maximum allowable emission (L. A. County) lbs./hr.	13.62
Ave. Wt. dust collected — lb./hr.	
in quencher	31.2
in secondary cooler	6.4
in dust collector	47.3
Total	84.9
Dust emitted from collector exhaust lb./hr. (thimble test)	0

ent alloys being melted, the operation of the furnaces may be intermittent, some not being used more than once a week. If all are connected to a single collector, needless horsepower is used during furnace stand-by time. If each furnace is connected to its own collector; equipment, space and cost may be prohibitive.

Foundrymen have installed conventional wet collectors, orifice scrubbers and bag filters on electric furnaces. The first 2 types show an efficiency on electric furnace fume of between 70 to 80%. Where bag filters have been used, there are no visible solids in the effluent.

Phosphorizing of Copper

When molten copper is inoculated with white phosphorus, dense clouds of phosphoric acid anhydride (P_2O_5) are given off. Because the anhydride is very hygroscopic and is often used for drying gases, it would seem that a wet-type collector would do a satisfactory job of fume collection. However, foundries engaged in the manufacture of phosphor copper have found it necessary to pass the fumes through a wet scrubber followed by electrostatic precipitation in order to obtain satisfactory collection and minimize corrosion.

Inoculation of Iron with Magnesium

Nodular iron was formerly made by inoculating iron with magnesium. During the inoculation process there is a sudden and violent generation of large amounts of iron and magnesium oxide, because the reaction is exothermic. Magnesium yields on burning about 11000 Btu./lb. Normally as much as 25 lbs. of magnesium/ton of iron are used, the volatilization loss of magnesium being as much as 97%.

In order to reduce the amount of resulting air pollution, foundrymen now inoculate iron with a nickel-magnesium alloy in an inert atmosphere of argon. This method results in an almost complete elimination of metal fumes and melting losses.

The Carbon Dioxide Process

More and more foundrymen are adopting the carbon dioxide process as a method of hardening cores and molds. In this process carbon-dioxide gas is introduced into the mold or core made from a mixture of sand and water glass ($Na_2 SiO_3$). This results in the precipitation of silica in the form of a gel and produces immediately stiffening or setting of the adhesive. The chemical reaction can be expressed by the following equation (as an approximation only):

$$Na_2 SiO_3 + H_2O + CO_2 = Na_2 CO_3 + Si O_2 + H_2O$$

The process replaces the customary method of baking cores and molds in ovens thereby completely eliminating not only the ovens but the fumes emitted from their stacks.

The foundry industry has passed from an art to a science, and foundry research is constantly going on. New methods and materials are being sought which will not only improve the product but will also control or eliminate air pollution. This is a wise approach since collected foundry effluents have no market value and collection equipment is a nonproductive investment.

However, since melting with cupolas is the cheapest way, it will be a long time before they will be supplanted by melting methods, emissions from which are lesser or cheap to control. Meanwhile, foundrymen must continue to select cupola collection equipment most suitable for their requirements.

Versatility of Oxidation Catalysts For Industrial Air Pollution Control*

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The principle of catalytic oxidation for controlling odors and visible emissions from various industrial processes is well known among authorities on air pollution. Numerous papers on the subject have already been published, of which several were presented at previous meetings of the Air Pollution Control Association[1]. Consequently, for the purpose of this paper, it suffices to state that catalytic oxidation is a combustion process which offers certain advantages over other methods of combustion in terms of efficiency and temperature requirements for oxidizing contaminants exhausted from industrial stacks.

Generally speaking, catalytic installations are usually associated to waste gases which are relatively free of so-called catalyst poisons, such as metallic oxides and other non-combustible contaminants. Specifically, in applications to industrial drying ovens for paint baking, wire coating, investment casting, and others, the effluents are found to be composed essentially of a mixture of air and pure hydrocarbons or other gases which can be oxidized completely to CO_2 and H_2O. It would be erroneous, however, to believe that catalytic oxidation must be limited to these simple and ideal applications. The problem of catalyst contamination can, in many cases, be resolved through engineering and the use of appropriate catalytic elements. The purpose of this paper is to discuss a number of successful cases where catalysts are being used in the presence of materials generally believed to be deterrents to catalytic oxidation.

* Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

In order to best understand the logic behind the design and operating conditions, it is necessary to analyze briefly the phenomenon of catalytic oxidation. It is generally accepted that the combination of molecules of the combustible gases and oxygen takes place at the surface of the

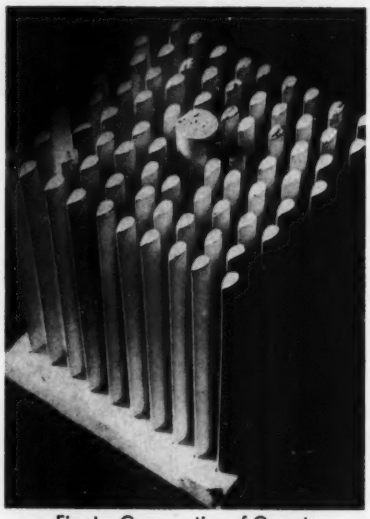

Fig. 1. Cross section of Oxycat.

catalyst. The rate at which this phenomenon occurs determines the activity of the catalyst. The physical and chemical characteristics of catalytic surfaces have an important bearing on the relative activity or rate of reaction of different catalysts. Recognizing this basic fundamental, it is obvious that to realize a successful catalytic oxidation reaction, the following factors must be considered:

(1) Precautions must be taken to minimize deposits on the catalytic surface, or clogging, in order to maintain contact with the molecules of combustible gases and the oxygen.

(2) The catalytic agent must be extremely active and applied uniformly to the carrier. A deposit or coating is less apt to hinder the reaction on a very active catalyst surface than on one which is less active.

(3) The catalytic element must be designed in such a way as to permit an even and equal flow over the catalyst surface and through the bed. If there is an entrainment present in the stream, there is less chance of clogging and contamination by maintaining equal velocity and even distribution of the gas flow. This also minimizes the problem of erosion of the catalyst surface since this condition can occur when the catalyst surface is exposed to an excessive gas velocity when the gas contains abrasive particles.

From the above, it is clearly demonstrated that the role of the catalyst itself in resisting contamination or poisoning cannot be overemphasized. As stated above, a very active and stable catalyst is able to withstand the presence of contaminating agents far more efficiently than one which is less active. By actual experimentation and in commercial installations, it has been shown that one catalyst will function satisfactorily for several thousand hr.; whereas, another form of catalyst will be poisoned in a matter of a few hr. under the same conditions. It is extraordinary to note

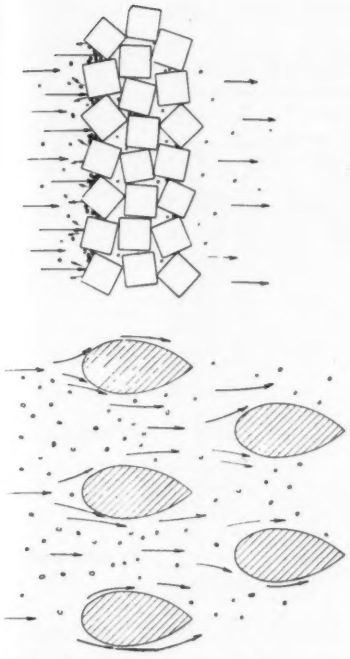

Fig. 2. Flow patterns for particulate matter.

that the difference in the behavior of catalysts can be so great when the catalysts are composed of the same basic elements but of different preparation or configuration. The correct proportion of the chemicals and metals which enter into the preparation of the catalytic agent is vital to obtain optimum catalyst activity. Equally important is the design of the catalyst carrier.

The catalytic element used on the installation described herein is what is commercially known as the Oxycat. In the composition and design of this element, detailed consideration has been given in the preparation of this catalyst to obtain the desired characteristics already described.

Fig. 1 shows a cross section of one of these elements. It consists of 2 porcelain end plates holding in place 71 porcelain rods evenly staggered in the unit. The unit measures $5\frac{1}{2}$ in. long, $3\frac{3}{16}$ in. high, and 3 in. wide. The rods are spaced at approximately $\frac{1}{4}$ in. intervals. This permits passage of solid particles up to $\frac{5}{32}$ in. through the bed without clogging. The rods are also streamlined in the form of neutral air foil to reduce turbulence, thereby minimizing back pressure and assuring a maximum surface contact with the gas stream. An equally important factor is the theoretical behavior of aerosols and other small particles in passing over an air foil section. Whereas such particles would normally impinge on the surface, due to the teardrop design they flow in a pattern similar to the gas molecules and pass over the surface without impinging (Fig. 2).

The catalytic agent of the Oxycat is a combination of platinum and alumina. The proportion of platinum and alumina used is a result of an extensive study and research program. Eliminating 1 of these elements, or changing the proportions to any degree, will radically reduce the activity and durability of the catalyst. The porcelain used in the carrier is a high grade spark plug-type which was selected because of its strength, chemical inertness, and resistance to high temperatures. The design and composition of the Oxycat permits operating temperatures as high as 1800°F which, in itself, is a feature that has greatly extended the possible fields of application. The configuration and dimensions of the Oxycat enable the stacking of these units side by side

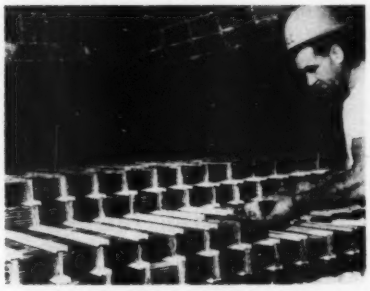

Fig. 3. Oxycat bed.

and in layers to form catalytic beds of any size (Fig. 3).

The first installation under consideration is one in which a resinous binder is applied to rock wool or Fiberglas. The material is then introduced into an oven where the binder is cured. In this curing operation, resinous materials are emitted which create an air pollution problem. The oxidation of these combustible resinous contaminants can readily be accomplished by catalytic oxidation. However, entrained in the exhaust stream, there are threads of the rock wool or Fiberglas which can cause plugging of the oxidation catalyst. A schematic flow diagram of this installation is shown in Fig. 4.

After passage through the exhaust fan, the effluent is heated by means of the preheat burner and passed through the Oxycat bed. Between the preheat burner and the catalyst bed, 2 stainless steel screens are installed in series to take out the major part of the entrained threads. These screens have been constructed so that they are easily removed for cleaning. The screens are located after the preheat burner since, at this point, the combustible contaminants are in a vapor state and readily pass through the screens; therefore, the deposit is accumulated on the screens as dry Fiberglas material which is easily removed. However, a certain percentage of the threads do pass through these screens but the design of the Oxycat allows passage of most of the remainder of the material. In actual installations, it has been found that there may be sufficient accumulation of fibers on the catalyst to necessitate cleaning the catalyst every 2 or 3 months. Other forms of catalyst would become ineffective in a matter of days. The elements here, however, can be cleaned without being removed by blasting compressed air through the bed. For this reason, it is desirable to design the catalyst chamber so that the catalyst bed is readily accessible either for removal or cleaning.

A second application is in connection with catalytic cracking plants. Catalytic cracking is a process which has been widely adopted by the oil industry to make high octane gasoline. The gases from the regenerator, which are the waste gases, are rich in combustibles containing anywhere from 3% to 8% of CO, plus some hydrocarbons. At first glance, this seems like an ideal application for catalytic oxidation. However, the gases, in addition to the combustibles, contain varying amounts of cracking catalyst dust or beads which are composed essentially of special types of alumina and silica. These catalyst fines are not to be confused with the oxidation catalyst. They actually are small particles of cracking catalyst

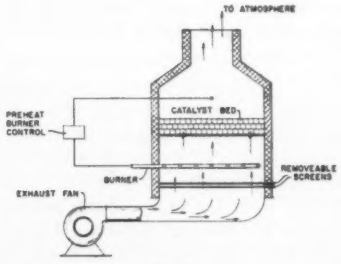

Fig. 4.

REGENERATOR FLUE GAS ANALYSIS

GAS FLOW @ 60°F 62,000 CFM (4630#)
TEMPERATURE OF GAS = 500°F
WET GAS ANALYSIS:

	MOL.%	WT.%
CO_2	8.3	13.0
CO	8.8	8.8
O_2	0.5	0.6
N_2	69.9	69.6
H_2O	12.5	8.0
	100.0	100.0

Air Added To Obtain O_2 For Combustion And Temperature Control - 4370# (58,000 SCFM)

BTU Available From CO	106,800,000	BTU/HR
BTU Available From Sensible Heat	30,000,000	BTU/HR
BTU Available From Preheat	90,000,000	BTU/HR
	226,800,000	BTU/HR

HEAT TO STACK @ 500°F	58,320,000	BTU/HR
RADIATION AND OTHER LOSSES	4,480,000	BTU/HR
	62,800,000	BTU/HR
NET HEAT TO STEAM	164,000,000	BTU/HR
NET STEAM PRODUCTION	160,000	#/HR @ 200 PSIG
TOTAL VOLUME IN SYSTEM	116,000	CFM @ 60°F

Fig. 5.

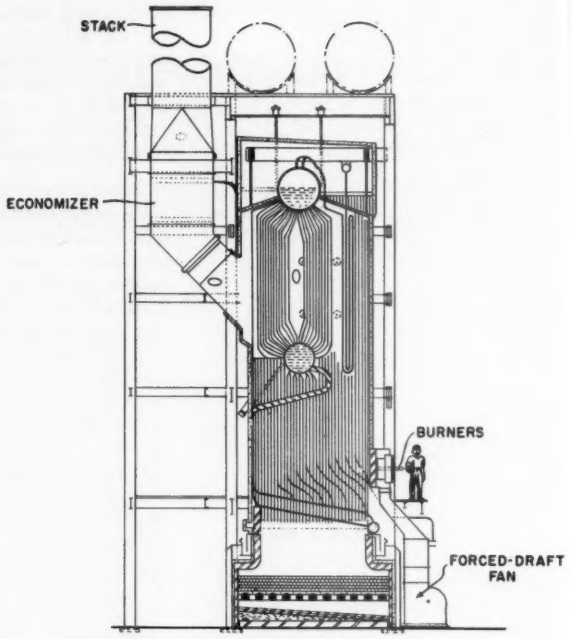

Fig. 6.

used in the catalytic cracking process. Cracking units are usually equipped with precipitators or cyclones which remove the major portion of the cracking catalyst carry-over before introducing the stream to an Oxycat system. Even with the most effective separators, a certain quantity of fines pass through the Oxycat bed. The physical characteristics of the Oxycat permit passage of the fines without adherence to the surface but the extremely abrasive nature of these fines demands careful precautionary measures against erosion of the catalyst surface. The design of the catalyst carrier makes possible an even flow through the bed and, consequently, the velocity of the gases can be maintained comparatively constant throughout the various sections of the catalytic mass. Erosion is, therefore, solved by engineering the installation to realize an even and low velocity of the gases over the catalytic surface. These installations are designed for a maximum rate of flow of 25 ft./sec.

Fig. 5 shows a typical analysis of gas stream. Since the gases from the regenerator are deficient in oxygen, air must be added to supply the oxygen for complete combustion of the CO and hydrocarbons. After mixing, the gas and air mixture may necessitate preheating to reach a minimum temperature of 650°F. which is the temperature required in this particular application for the catalytic reaction to occur. The preheating is normally accomplished by line burners using refinery gas or oil as fuel. Following mixing and preheating, the gas stream enters the catalyst chamber through an inlet designed to disperse the stream uniformly throughout the bed. The catalytic oxidation reaction results in a temperature rise of 600°-900°F., bringing the final temperature of the gas stream emerging from the catalyst to 1300°-1600°F. This gas is then introduced into a waste heat boiler (Fig. 6) to generate steam required to operate the catalytic cracking unit or other equipment. The heat that can be generated from oxidizing the waste gases from some of the larger units is sufficient to raise as much as 300,000 lb. of steam/hr. The pay-off in terms of fuel recovery is extremely attractive —often less than 2 years, depending on local fuel costs. There are several installations of this type throughout the country, one of them having been on stream for over 2 years without any evidence of erosion or reduction in catalyst activity. While these installations are primarily for heat recovery, they also eliminate the objectionable plume which is usually associated with cat crackers.

The third example under discussion is one which is applied to carbon black manufacturing processes. These processes have tail gases which contain large quantities of combustibles. Entrained carbon black creates a considerable air pollution problem which may be the motivating force for such an installation. There, again, the economics are so attractive that these installations can also be justified for heat recovery alone. The heat generated is used to produce steam and can also be used to preheat the fuel from which the carbon black is made. A typical analysis of this tail gas is shown in Fig. 7.

You will note the high hydrogen and carbon monoxide content of these gases along with the lesser quantities of other combustibles. Fig. 8 shows the flow in such a system. Since the gases in this operation are deficient in oxygen, air is added to supply the oxygen required for catalysis. It is necessary to preheat this mixture since the waste gas is received at a temperature of approximately 300°F. The addition of air, of course, reduces this temperature somewhat. Experience has shown that a temperature of approximately 600°F. entering the Oxycat bed is required to maintain catalytic activity of these gases with the entrained carbon black. This is accomplished initially by means of the preheat burner installed on the upstream side of the Oxycat bed. After preheating to 600°F., the com-

WASTE GAS FROM CARBON BLACK PROCESS

GAS FLOW @ 60°F. 25,000 C.F.M. (1900#)
TEMPERATURE OF GAS 350°- 400°F
WET GAS ANALYSIS:

	MOL. %
H_2O	52.0
CO	5.76
CO_2	2.40
H_2	5.76
N_2	33.50
CH_4	0.37
C_2H_2	0.24
ORGANIC S	TRACE

Air Added To Obtain O_2 For Combustion. Plus 2% Excess - 845# (11,100 S.C.F.M.)

BTU Available From Combustibles In Stream	68,000,000 BTU/HR.
BTU Available From Sensible Heat	12,000,000 BTU/HR.
BTU Available From Preheat	15,600,000 BTU/HR.
	95,600,000 BTU/HR.

HEAT TO STACK @ 500°F.	22,400,000 BTU/HR.
RADIATION AND OTHER LOSSES	1,900,000 BTU/HR.
	24,300,000 BTU/HR.
NET HEAT TO STEAM	70,300,000 BTU/HR.
NET STEAM PRODUCTION	68,500 #/HR. @ 200 P.S.I.G.
TOTAL VOLUME IN SYSTEM	36,100 C.F.M. @ 60°F.

Fig. 7.

bustible vapors are oxidized within the Oxycats and a temperature of approximately 1600°F. is realized emerging from the catalyst. Some oxidation of the particulate carbon black is also achieved. However, there is no evidence to indicate that this is a catalytic reaction. It is merely the oxidation of carbon black due to its contact with a hot surface; in this case, the Oxycat. While virtually complete elimination of the combustible vapors is achieved in the catalyst, only about 40% oxidation of the carbon black is effected. To increase the efficiency of carbon black oxidation, checkerbrick is provided following the catalyst bed which, of course, assumes the stream temperature of approximately 1600°F., and presents a hot surface to complete the oxidation of carbon black. Continuous operation without the necessity of adding supplementary heat to increase the inlet temperature from 300°-600°F. can be achieved by recirculating a portion of the gases after catalysis and combining them with the tail gas/air mixture.

This is another case where the catalyst bed must be capable of long operation under high temperatures and other severe operating conditions. A very active catalyst is necessary to obtain an homogeneous catalyst skin temperature sufficiently high to burn almost instantaneously the carbon which deposits on the surface. A slow rate of burning would result in a build-up of carbon which would keep the molecules of gas from entering into contact with the catalyst surface and eventually kill the reaction.

The fourth example is one in which the tail gases from a phthalic anhydride process are catalytically oxi-

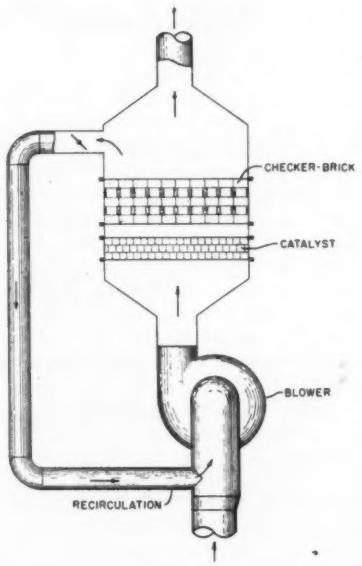

Fig. 8.

dized to eliminate an air pollution problem. These gases are at a low temperature and contain relatively small amounts of combustible materials which are, nevertheless, obnoxious. The carbon monoxide present in the stream represents the largest quantity of combustibles. CO, in itself, does not appreciably add to the air pollution problem. The main offenders are the other contaminants; phthalic anhydride, maelic anhydride, naphtha quinone, and formaldehyde. The formaldehyde generally is the one that is most objectionable to the average person. In this type of installation, oxidation is achieved at a catalyst inlet temperature of approximately 650°F., the outlet from the catalyst being approximately 750°F. The difference is achieved by oxidation of the combustibles. The carbon monoxide is a material contributor to this 100°F. increase. A flow diagram of such an installation is shown in Fig. 9. In this system, a portion of the preheat requirements for the catalyst bed are obtained by the use of a heat exchanger. Another interesting engineering feature is the provision for returning a portion of the preheated gases back to the system to increase temperatures of the waste gas to a minimum of 225°F. This is necessary to prevent corrosion of the heat exchange surface due to the acids present in the stream. Here,

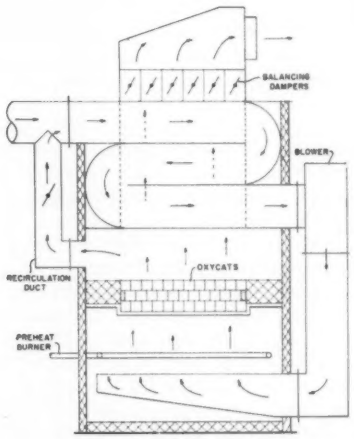

Fig. 9.

again, the catalyst must be designed to withstand long operation without a reduction in catalyst activity. The gases usually contain aerosols as well as some iron oxide and sulfates resulting from the highly corrosive effect of the gases on the system. Unless the catalyst has a very high activity level, these contaminants are sufficient to reduce the efficiency of the system in a very short time. Oxycats have functioned on a typical phthalic anhydride waste gas stream for 2 years without appreciable reduction of activity or necessity of cleaning even

though inspection of the bed after 18 months showed evidence of the penetration of the aerosols and a deposit of iron sulfate. For this and most applications involving complex gas streams, the catalyst should not be exposed to the stream below operating temperature. The catalyst surface can be damaged by an excess of condensible deposits, such as resins and other carbonaceous materials. This condition is easily avoided by using a damper arrangement and by-passing the catalyst until the system has reached a minimum temperature.

The use of oxidation catalysts for air purification is not new but much progress has been made with reference to applying the principle for industrial use. New avenues are constantly being explored and, as demonstrated, many industrial odor problems caused by organic or combustible contaminants are being solved catalytically, regardless of the complexity of the process streams, through proper engineering and application. Before these new techniques were developed, such installations were often considered impractical due to excessive costs as a result of frequent catalyst replacement and other operating difficulties. Air pollution control equipment can only be successful if designed and built to operate with the same efficiency and reliability as other plant equipment.

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Sources and Control of Sulfur-Bearing Pollutants*

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Gaseous sulfur-containing pollutants were early recognized as undesirable contaminants of the atmosphere, giving rise to damaging effects to man, animals, vegetation, and structures. It was not difficult to determine some sources of these pollutants, and significant improvements have resulted from adoption of technological countermeasures. Progress has been greatest for industries where the concentrations of sulfur compounds in waste gases is highest, such as smelters, and where it has been found that the recovered by-products can pay their way. Less progress has been made in combatting the effluent problem of sulfur compounds resulting from the combustion of fuels, where the concentration of sulfur compounds in the stack gases is low but where the total amount emitted is largest.

It was estimated[1] in the mid 1940's that almost 40 million tons of sulfur were being emitted annually into the world's atmosphere from the combustion of coal, the smelting of ores, and the production and consumption of petroleum and natural gas. This amount must now be exceeded by a significant margin, since the world production and consumption of the raw materials concerned has increased, and since there is some evidence that the average sulfur content of fuels is also increasing. Although the volume of sulfur compounds, chiefly sulfur dioxide, represented by this release of sulfur is enormous, the volume of air in the atmosphere is so much larger that there is little danger of raising the average concentration of sulfur dioxide to a level detrimental to man or his environment if uniform dilution were possible. It is in the special circumstances of sulfur emission where higher concentrations are brought about by reason of geographical and meteorological conditions that detrimental effects are observed. Also, the sulfur dioxide does not remain in the air but reaches the earth eventually in other forms.

Sulfur-Containing Pollutants

Sulfur dioxide, sulfur trioxide, and hydrogen sulfide are the three principal sulfur-containing pollutants. Hydrogen sulfide is listed here as a primary pollutant, although it usually is burned to form sulfur dioxide and water vapor before being vented to the atmosphere. In addition, a variety of other sulfur-containing organic compounds are emitted to the atmosphere, such as mercaptans, but these represent but a minute fraction of the total. The high odor level of these substances in the immediate location of the plant, even though the actual concentration is low and has no toxic effect on man or his environment, places such substances in the classification of a nuisance.

By far the greatest proportion of the sulfur compounds emitted to the atmosphere is in the form of sulfur dioxide. This form is produced from the smelting of ores of metals such as zinc, lead, copper, and nickel, from the combustion of gases from refinery and natural gas waste products, and from the combustion of oil and coal. The effects of sulfur dioxide on vegetation, on the corrosion and disintegration of structural materials, and on the physiological effects on man have been under investigation for many years. In low concentrations, up to 0.10 to 0.20 ppm., there appears to be no adverse effects of sulfur dioxide on plants and vegetation. In fact, in certain instances, there may be a beneficial effect resulting from its presence since sulfur dioxide supplies sulfur essential to plant growth. At concentrations of 0.25 to 0.40 ppm. and above, sulfur dioxide can be injurious to vegetation.

Corrosion of materials and structures as a result of exposure to gases containing sulfur oxides is an associated factor. This is apparent in inplant structures which are subjected to significant concentrations of the oxides. Damage to cloth materials and clothing has also been cited as one of the more subtle aspects of the disintegrating effect of sulfur oxides present in the atmosphere of some dwelling areas. Corrosive damage of this kind can be appreciable in municipalities located in areas where geographical and meteorological conditions are unfavorable to the dispersion of industrial waste gases and combustion products.

The physiological effect of sulfur dioxide and its oxidation products on human beings is centered on the irritating effects produced in the respiratory system. The lowest detectable odor level for sulfur dioxide is about 3.5 ppm., and the tolerable limit for prolonged exposure is about 10 ppm. It will be noted that the levels mentioned are far above the levels of tolerance for growing vegetation. Hence, if measures are taken to avert damage to plants, man is also effectively relieved of adverse effects. To sum up, the limits of concentration for sulfur-containing gases for prolonged exposure by man have been stated to be about 10 ppm. for sulfur dioxide, 1 ppm. for sulfur trioxide, 2 to 10 ppm. for sulfuric acid, and 20 ppm. for hydrogen sulfide. McCabe[2] has recently discussed these factors in a review of the significance of sulfur dioxide as a pollutant material.

With the formation of sulfur dioxide in combustion processes, a small quantity of sulfur trioxide is also formed. Of the total sulfur oxidized, less than 10% may be oxidized to SO_3 and the SO_3 is usually of the order of 1% of the sulfur dioxide present. This sulfur trioxide may hydrolyze in the atmosphere to produce sulfuric acid mist. The particle size of the sulfuric acid mist varies from 0.5 to 6 μ depending upon the amount of water vapor present. It has been reported that an aerosol containing 1600 particles/cm.^{3} of 0.5 μ diam. will reduce visibility to 3 miles[3]. Studies by Gerhard and Johnstone[4] indicate that sunlight induces oxidation of SO_2 to SO_3. This phenomenon adds to the severity of the pollution effects by sulfur dioxide.

* Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

Sources of Sulfur Emissions

The principal sources of sulfur contaminants in the atmosphere, in order of decreasing amounts are as follows:

(1) The combustion of coal.
(2) The production, refining, and utilization of petroleum and natural gas.
(3) Industries making and using sulfuric acid.
(4) The smelting and refining of ores, principally copper, lead, zinc, and nickel.

Fig. 1 presents estimates of sulfur emitted to the atmosphere of the United States from the four sources outlined above. In general, those industrial operations emitting the least sulfur to the atmosphere are those in which the sulfur dioxide concentration in the waste gases is also the highest. Thus, the combustion of coal is responsible for the heaviest contamination of the atmosphere by sulfur dioxide although the sulfur dioxide concentration in the effluent gases from this process is the lowest —less than 1%.

Table I presents the sulfur content of various mineral fuels, both raw and refined. The maximum allowable concentrations of sulfur in the light refined fuel oils, gasoline, diesel oil, liquefied petroleum gases and natural gas distributed by utilities is defined by standards set by government and industry. The sulfur content of coal and heavy fuel oil is subject only to agreement by buyer and seller. In a few instances, however, the maximum sulfur contents of fuel burned within certain geographical areas are limited by law.

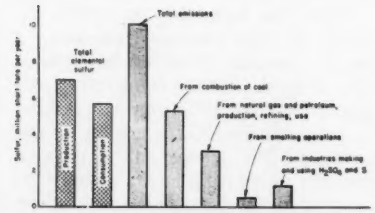

Fig. 1. Estimated emission of sulfur in the atmosphere, in the United States, 1953 (After McCabe)[2].

Since the combustion of coal is responsible for the largest pollution of air by sulfur-containing materials, it is of interest to review the forms of sulfur in coal. Sulfur is present in coal in varying amounts, ranging from a trace to as much as 10% or more in extreme cases. Although the sulfur content of most prepared commercial coals will not exceed about 2.5%, some of those used by power plants will contain as much as 6%. There does appear to be a trend toward increasing sulfur content in mined coal.

TABLE I
Sulfur Content of Some Mineral Fuels

Type of fuel	Sulfur, % by weight
Solid	
Bituminous coal	0.3-6.0
Common range	0.7-2.0
Anthracite	0.6-1.0
Metallurgical coke	1.0
Wood	Negligible
Liquid	
Crude petroleum	0.2-1.7
Fuel oil, No. 6	0.3-3.0
Fuel oil, No. 2	1.0 (max. specification)
Diesel oil, 1-D	0.5 (max. specification)
Gasoline	0.01-0.4
Gaseous	
Liquefied petroleum gas	0-25 gr./100 ft.[3]
Manufactured gas	2-10 gr./100 ft.[3]
Natural gas	0-10 gr./100 ft.[3]

The sulfur in coal does not occur in the free state, but is present in combined form with the coal substance and with mineral matter. That in combination with coal substances is referred to as organic sulfur. It cannot be separated by mechanical cleaning processes. The proportion of the total sulfur in the organic form varies widely in different coals.

The inorganic portion of sulfur includes pyritic and sulfate forms. The sulfate sulfur may be present as calcium sulfate, or in weathered coals as ferrous sulfate which has been formed as a result of oxidation of the pyrite. The amount of the sulfate present in freshly mined coal is usually negligible, although appreciable percentages may be present in high sulfur coals that have been stored for some time. Pyritic sulfur is present as pyrite, FeS_2, or as marcasite which has the same chemical composition but differs in crystalline form. It is found as finely sized particles distributed throughout the coal substance, and as bands of various thickness along cleveage cracks and partings. Pyritic sulfur can, in some cases, be removed by cleaning operations. Thus, it is not uncommon to reduce the sulfur content of coals by as much as 25-35% by economically practical cleaning procedures.

When coal is carbonized to form metallurgical coke, approximately 60% or more of the sulfur in the coal remains with the coke which is then charged to a blast furnace or used in other operations. The smaller percentage of the sulfur that does not remain behind with the carbon or coke appears in the gaseous products from the coke oven. In most modern coke oven plants, this sulfur is recovered along with the rest of the materials from the carbonization process.

As an example of the problem of pollution offered by a coal burning power plant, consider one which discharges 1,000,000 cfm. of flue gas having an average concentration of approximately 0.28% by volume of SO_2. This represents an emission of roughly 190 tons/day of SO_2. These figures indicate the magnitude of the problem when considering sulfur emission from coal-burning equipment. The fact that the concentration of SO_2 in the effluent gas is considerably below 1% presents a challenging technological problem in attempts to reduce sulfur emissions.

The sulfur content of new crude petroleum discoveries in the United States and throughout the world is increasing. Improved refining processes, particularly the use of catalytic cracking of oils instead of thermal cracking, serve to increase the yield of distillate products/barrel of crude, and also to alleviate some of the problems associated with high sulfur crudes. In these newer processes, the high-boiling sulfur compounds contained in the feed oils are converted largely to hydrogen sulfide gas and to lower-boiling sulfur compounds. Fortunately, the concentration of hydrogen sulfide in the refinery gases is sufficiently high, 3.5 to 7% on an average, that it can be removed eco-

TABLE II

Example of Sulfur Balance for the Catalytic Cracking of a Gas Oil—(Feed stock: 2.5% sulfur, 25 API gravity)

Cracked products	Distribution of sulfur, %
Raw gas products, C_1 — C_4 fractions	36*
Raw liquid products:	
C_5 — 430 F gasoline	3*
Light gas oil	11*
Heavy gas oils to fuel	43
Coke, burned in regenerator	7
Total	100

* Sulfur compounds are removed from these products. Data from Air Pollution Handbook, McGraw-Hill Book Co., 1956.

nomically from the cracked products.

Table II presents a sulfur balance for a typical catalytic cracking operation.

From the distribution in Table II, it is seen that almost 40% of the sulfur in the feed stock will be contained in the gaseous products from the refinery. This sulfur, in the form of hydrogen sulfide, can be recovered economically.

It should be noted that the amount of hydrogen sulfide released per barrel of crude is increasing even as additional catalytic refining processes are being installed. This trend has one promising feature, in that the quantities of H_2S being produced in many refineries today are too large to permit flaring as SO_2. As a result, there is an increasing trend towards the installation of plants to convert the H_2S to elemental sulfur. This is a satisfactory solution to the problem both from a practical and economic standpoint. In population centers of the United States there were approximately 17 refinery plants converting H_2S gases to elemental sulfur in 1956[4]. For example, in the Los Angeles area, plants are recovering about 180 tons/day of sulfur which is equivalent to approximately 360 tons of SO_2; 120 tons are being recovered in the Houston area, and 165 tons in the Philadelphia area. All told, it was estimated that beginning in 1956, approximately 1000 tons of sulfur were being recovered daily from sour gases of petroleum refineries throughout the United States.

A typical example of the recovery of sulfur from petroleum refining operations is the plant of the McKee, Texas, Refinery of Shamrock Oil and Gas Corporation. This plant produces sour gas at a rate of 1900 MM ft.^{3}/day having a composition of H_2S, 43.0%; CO_2, 55.5%; and light hydrocarbons 1.5%. The gas is fed into the sulfur plant at 100°F. and a pressure of 3 lb./in.^{2} One-third of the H_2S is oxidized to SO_2 which is then reacted with most of the remaining H_2S over a natural bulk site catalyst to form elemental sulfur.

Sulfur emitted to the atmosphere from sulfuric acid making and using plants is usually in the form of SO_2. The problems faced by this segment of the industry are similar to those brought about by burning coal. Thus, the concentration of SO_2 in the tail gases is so low as to be uneconomical to recover.

Although the refining of ore, particularly nonferrous smelters, results in the emission of much SO_2 into the atmosphere, these smelters are usually located remote from population centers and contamination is a less serious problem than it might be. Sulfur compounds are contained principally with sulfide ores of lead, zinc, copper, and nickel. Fortunately, there are 2 possible means of reducing air pollution by sulfur-containing compounds from smelting operations. First, it is possible to control the ore concentration to a substantial extent so as to exclude much of the sulfur-bearing gangue. Secondly, successful processes have been developed to make it possible to recover useful by-products — sulfuric acid and sulfur — from many of these plants. This latter possibility exists because of the relatively high concentration of SO_2 in the effluent gases, which usually range from 1 to 6% or even higher.

The Recovery or Removal of Sulfur From Effluent Gases

The 2 principal gases containing sulfur for which means of recovery or removal from effluent gases are desired are hydrogen sulfide and sulfur dioxide.

Removal of Hydrogen Sulfide

Hydrogen sulfide is produced in the coking of coals and in petroleum refining operations, and is present in many natural gases. Many of the hydrogen sulfide removal and recovery plants have been installed for the special purpose of eliminating atmospheric pollution.

A large number of processes for the removal of hydrogen sulfide from various gases have been developed over a period of the last 20 years. Two of these processes, the catalytic conversion process and the Girbotol process have been widely applied in recent years for sour natural gas and refinery gases.

Catalytic Conversion Process

This is a process currently being installed extensively to recover H_2S at petroleum refineries. Fig. 2 shows a simplified flow diagram of the process. This process consists of converting H_2S to elemental sulfur by controlled combustion with air. Approximately ⅓ of the hydrogen sulfide is burned to form SO_2 which reacts with the remaining ⅔ of the H_2S to form sulfur and water vapor. The reactions are as follows:

$$2\,H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$
$$2\,H_2S + SO_2 \rightarrow aS_2 + bS_6 + cS_8 + 2H_2O$$

The letters a, b, and c represent the number of moles of the various molecular forms of sulfur formed. A bauxite catalyst is used to promote further reaction of the H_2S and SO_2. The sulfur vapor is condensed and recovered as liquid sulfur.

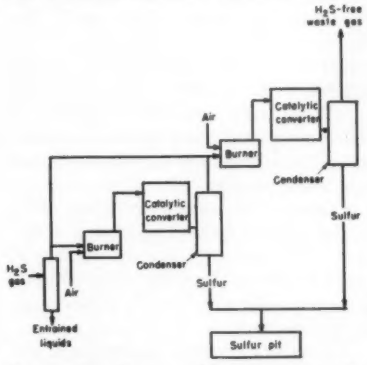

Fig. 2. Flow diagram of catalytic conversion process for recovering H_2S from waste gases.

Girbotol Process

This process was first used in 1929 and since has been installed in hundreds of plants. By this method, the raw gas is passed upwardly through the bubble-tray absorber solution. The absorbing solutions may be solutions of monoethanolamine or diethanolamine. The absorbent solution then flows through heat exchangers to a second bubble plate tower or

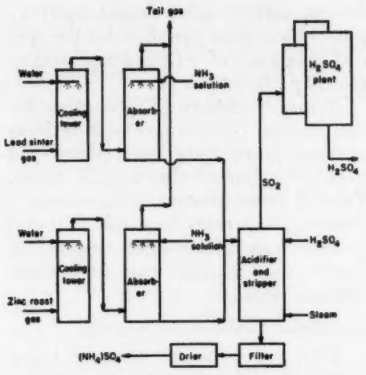

Fig. 3. Simplified flow sheet of ammonia process used at Trail, B.C., to recover SO_2 from smelter gases.

reactivator, where the hydrogen sulfide is stripped from the solution by steam.

Other processes for the removal of hydrogen sulfide from effluent gases include the Thylox process, phenylate or Alkazid process, tripotassium phosphate process, Seaboard process, and the iron oxide-drybox system.

Removal of Sulfur Dioxide from Smelter Gases

Only 1 physical method of recovering sulfur dioxide from effluent gases has been reported. Schnell[5] describes a refrigeration process to recover SO_2 from roaster gas containing 6.5 to 7.0% SO_2. Ammonia and sulfur dioxide are the refrigerants used to cool the waste gases after they have been compressed to a pressure of 5.5 atmospheres.

Chemical processes in which SO_2 in the effluent gases reacts with a liquid absorbent are most commonly considered for treating SO_2-containing gases, and much work of this type has been done.

The use af aqueous ammonia to absorb SO_2 from effluent gases has been investigated extensively. Essentially, SO_2 is absorbed by the following reaction:

$$SO_2 + 2NH_3 + H_2O \rightarrow (NH_4)_2SO_3$$

$$SO_2 + NH_3 + H_2O \rightarrow NH_4HSO_3$$

Carbon dioxide associated with the SO_2 is not absorbed since the solution is acid, a pH of less than 5.5 usually being used. The absorbed SO_2 can be recovered by acidifying the solution with sulfuric acid and steam stripping. This is the process used at Trail, British Columbia[6], where substantially 100% SO_2 is recovered from lead and zinc roaster gases. Fig. 3 shows a simplified flow sheet of the Trail process. Also, the solution could be treated with sulfuric acid and heated under pressure in an autoclave to produce ammonium sulfate and elemental sulfur.

One serious disadvantage in the use of ammonia is the high vapor pressure of this material and its loss in the scrubber. However, it appears possible to reduce and control this loss to a minimum. Johnstone and West[7] suggest the use of a cooling tower immediately ahead of the scrubber to cool the flue gases to their adiabatic saturation temperature. This coupled with the use of a multi-stage scrubber using solutions of less concentrated ammonia as the gases are freed of SO_2 results in better efficiency of SO_2 removal to reduce loss of ammonia. However, at the same time it does increase the capital investment required for the recovery operation. At Trail, loss of ammonia is controlled by adjustment of the pH.

The use of aromatic amines as absorbents for sulfur dioxide has been studied extensively both in the United States and Germany. Dimethylanaline, diethylenetriamine, triethyltetraamine, ethylamine, diethanolamine, and mixtures of pyridine, quinoline, isoquinoline, acrildine, aniline, xylidine with lactic acid, citric acid, glycerol, ethylene glycol, diethyl glycol, and water have been studied. Two processes using amines have been developed on a commercial scale, the dimethylaniline process used by the American Smelting and Refinery Company at Selby, California[8], and the xylidine or sulfidine process developed in Germany[9] using a suspension of xylidine or toluidine in water. In both processes the absorbed SO_2 is recovered by steam stripping. Fig. 4 presents a simplified flow sheet of the dimethylaniline process used at Selby.

Because of the high vapor pressure of dimethylaniline and its low absorption capacity for SO_2 at high temperatures, it is usually necessary when treating sulfur-containing gases to cool the gases to at least 85°F.; hence, a large cooling tower is required. In addition, water which would form a complex with dimethylaniline must be removed before scrubbing the SO_2-containing gases. The absorption of SO_2 by dimethylaniline produces enough heat that arrangements must be made to cool the absorbent during scrubbing. At Selby this is done by intercoolers between bubble trays.

The xylidine process was developed by the Lurgi Company and was used at 2 plants in Germany. Upon absorbing SO_2, the absorbent becomes homogenous, changing from a suspension of xylidine in water to a solution. Xylidine has a greater absorbing capacity for SO_2 than does dimethylaniline when treating gases containing less than 1% SO_2. The biggest disadvantage of xylidine stems from the auto-oxidation of dissolved SO_2 to form a solid reaction product. With dilute gases this becomes increasingly serious and solids may block the passages within the scrubber. The sulfate can be removed in a separate cycle as in the dimethylaniline process, but solid products are likely to form in the scrubber.

The Removal of Sulfur Dioxide From Power Plant Gases

Fig. 1 showed that the combustion of coal and heavy fuel oils represent the largest source of sulfur-containing air pollutants. The concentration of SO_2 in the gases emitted from boiler plants, the largest use of coal and heavy fuel oil, is less than 1% and usually of the order of 0.1 to 0.2% by volume. Thus, removal of SO_2 from these gases to control air pollution presents a challenging problem. In addition, much of the coal consumed in the U. S. is burned within or adjacent to large population centers where the resulting contamination of the atmosphere may be objectionable.

At the present time there is only 1 process, installed at 2 power stations, in use for the treatment of effluent gases from large boilers burning coal. The process was first installed at the Battersea Power Station in London, and is termed the *Battersea* process. This installation and the one at the Bankside Station in London were put in as a result of public opinion in England in 1929 following a series of

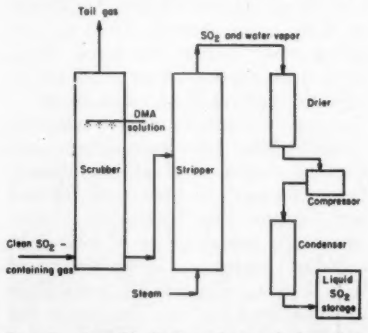

Fig. 4. Simplified flow sheet of dimethylaniline process for recovering sulfur dioxide.

exceptionally severe smogs. The original Battersea installation treated the effluent gas from coal burned with an average sulfur content of 0.88% in such a fashion that only 9% of the sulfur escaped into the atmosphere. The process is relatively simple and takes advantage of the fact that the River Thames, which supplies the water for scrubbing the flue gases, already contains most of the alkali that is required to neutralize the sulfur dioxide in the effluent gases. In addition, the river carries away the product, calcium sulfate, in solution. Thus, use of the process was favored by natural conditions.

Fig. 5 shows a flow sheet of the Battersea process. Essentially, the flue gas is washed with a slurry of chalk (calcium carbonate) on grid scrubbers; only enough chalk is added to the river water to maintain an alkalinity required to neutralize the SO_2 in the effluent gases. Crude manganese sulfate is added to the effluent to activate the oxidation of sulfide in the aeration tank. The solution from the scrubber passes to a settler and into an oxidizing tank before being sent to the river. At the present time the cost of this process is in the range of 12 to 15% of the cost of delivered coal.

The Howden I.C.I. cyclic lime process was tried for a time at the Tir John Power Station in Swansea, Wales, England, and at the Fulham Power Station in London. Essentially, this is a cyclic process similar to that used at the Battersea Power Station except that in this process calcium carbonate is concentrated and discharged as a wet mud. The scrubbing solution is essentially the same as used at Battersea, a slurry of the cheapest alkalis, chalk and lime. It has been estimated that use of the process would cost about 25% of the cost of the coal consumed at a large central station power plant. In this process as well as the one at Battersea the SO_2 is not recovered in saleable form. Most other development work has been directed towards processes which would yield a commercial product as an operating credit.

The possibility of producing sulfuric acid, either concentrated or dilute, directly from SO_2-containing power plant gases has been investigated. Johnstone[10], as part of a long-range program on the removal of SO_2 from such flue gases, studied the catalytic oxidation of SO_2 absorbed in water to produce sulfuric acid. He found that iron and manganese increased the rate of oxidation of SO_2 in solution and that dilute sulfuric acid could be made. Although 40% acid was made for short periods of time, the action of the catalyst was soon inhibited by phenols and copper salts. Recent work[11] has extended this study to include the use of ozone to oxidize the SO_2. It was shown that flue gases containing 0.35% by volume of SO_2 could be treated with air containing ozone and then scrubbed with a dilute solution of H_2SO_4. The cost of the ozone required/ton of recovered H_2SO_4 was estimated to be $5.00.

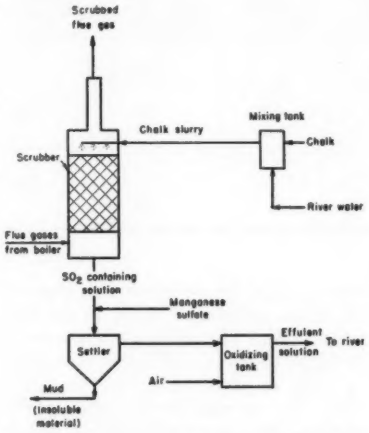

Fig. 5. Diagrammatic flow sheet of the Battersea process for treating power plant gases.

A *zinc oxide regeneration* process for possible use in power stations was developed at the University of Illinois by H. F. Johnstone[12] and co-workers. Essentially, SO_2-containing gases are washed with an aqueous solution of sodium sulfite and bisulfite, and the SO_2 is absorbed by the following reaction:

$$SO_2 + SO_3— + H_2O \rightarrow 2HSO_3—.$$

A portion of the bisulfite formed is recirculated, which accounts for the bisulfite in the absorbing solution.

The SO_2-containing solution is treated with zinc oxide to precipitate hydrated zinc sulfite, and the original solution is regenerated according to the equations:

$$ZnO + NaHSO_3 + 2\tfrac{1}{2}\ H_2O \rightarrow ZnSO_3 \cdot 2\tfrac{1}{2}\ H_2O + NaOH$$

$$NaOH + NaHSO_3 \rightarrow Na_2SO_3 + H_2O.$$

The addition of the zinc oxide results in removing the SO_2 dissolved in the absorber as zinc sulfite, and, at the same time, restores the original sulfite to bisulfite ratio. The hydrated zinc sulfite is filtered from the solution, dried, and flash calcined. The gases evolved from the calcining consist of water vapor and SO_2. The zinc oxide recovered is ready for reuse.

The capacity of the absorbent, sodium sulfite, is high and the solution has the advantage of having a negligible vapor pressure of SO_2 at temperatures as high as 130°F. (54°C.); thus, it is not necessary to cool the flue gases before entering the scrubber and the loss of the absorbent comes only from spillage and handling. As in all processes in which SO_2 is absorbed into a solution, a portion, almost 10%, is oxidized to SO_3 and forms sulfate ions. These must be removed since they neutralize sodium ions otherwise available for neutralizing absorbed SO_2. To eliminate sulfate ions, a portion of the effluent scrubbing solution is withdrawn from the main stream. Both fly ash and a portion of the sulfate in the main stream are withdrawn. This portion of the solution is treated with lime and SO_2 to precipitate calcium sulfate which is filtered from the treated solution. The solution free of calcium sulfate can then be sent back to the main stream of scrubbing solution.

The process is complicated by the necessity for removing sulfate and has not been used in a full-scale plant.

Efforts have also been made to adopt the Trail ammonia process for smelter gases to the scrubbing of the more dilute SO_2-containing gases from power plants.

A modification of the Trail process for possible use at power stations is the Autoclave process. The SO_2-containing gases are scrubbed with an ammonia solution, and the resulting SO_2-containing solution is treated with H_2SO_4 in an autoclave, producing $(NH_4)_2SO_4$ and elemental sulfur.

At present, none of the processes described appear to be economic for use with boiler plant stack gases.

The authors recently made some estimates of the engineering requirements for removing sulfur dioxide from a foreign power station burning coal containing 9% sulfur. This sulfur content is considerably higher than coals known to be used in U. S. practice. The station under consideration burned 220,000 tons of coal/year, which resulted in the emission of approximately 32,600 tons of SO_2 to the atmosphere, assuming a small loss of sulfur in the ash. With approximately 20% excess air, the con-

TABLE III

Comparison of SO_2 Recovery Process for Use at a Coal-Burning Power Station—(Size of Station, 220,000 Tons of Coal/Year Containing 9% Sulfur)

	Process				
	Zinc Oxide Regenerative	Trail	Autoclave	Dimethyl Aniline*	Xylidine*
Investment	1,752,000	2,376,000	1,746,000	2,000,000	2,000,000
Operating Cost/Yr.	965,000	1,552,000	1,471,000	1,688,000	1,917,000
Products, tons/Yr.					
Liquid SO_2	26,300			26,300	26,300
$(NH_4)_2SO_4$		37.200	39,200		
S			5,500		
H_2SO_4		16,750			
Value of Products, dollars/Yr.	325,000	1,558,000	1,390,000	325,000	325,000
Utilities					
Kwh/day	9,600	8,800	5,600	93,600	40,000
Water, gal./day	150,000	1,500,000	860,000	2,000,000	2,000,000
Steam, lb./day	—	362,000	240,000	1,200,000	440,000
Chemicals Required, tons/day					
NH_3		26.6	27.65		
H_2SO_4		65.5	3.83	48	46
ZnO	1.3				
Na_2O	5.62				
CaO	6.76				
NaOH					50
Na_2CO_3				42	

* Only roughly estimated.

centration of SO_2 in the flue gases was estimated to be 0.6%.

Estimates of the economics of the following processes were made for this station: (1) the zinc oxide regenerative process, (2) an ammonia process similar to that used at Trail, B. C., (3) the autoclave process, (4) the dimethylaniline process, and (5) the xylidine process.

Table III presents a comparison of these processes. It can be seen that even for a station emitting gases with a relatively high concentration of SO_2, 0.6%, only those processes using ammonia scrubbing showed a possibility of being economically feasible. It should be noted that these figures require further refinement to be generally applicable, since the possibility of SO_2 recovery was only a part of the study conducted and only estimates were prepared for equipment costs.

The Trail process cost includes a sulfuric acid plant of 50 tons/day capacity. The equipment for handling the flue gas is the same for both the Trail process and the autoclave process, except that an autoclave and ball mill are substituted in the latter for the acidifier, steam stripper, and H_2SO_4 plant.

The dimethylaniline process would require cooling of the flue gases to 85°F., using a cooling tower larger than the absorption tower for the Trail process. In addition, a coke filter would be necessary to remove all of the condensed water in the flue gases. The absorption tower would be large because of the low solubility of SO_2 in dimethylaniline and the need for scrubbing to recover dimethylaniline vapors. Xylidine, which has a greater capacity for SO_2 than dimethylaniline, would reduce the power and steam requirements as shown in Table III.

From available information, it is obvious that the control of SO_2 emitted from power plants using high-sulfur fuels presents a serious problem, and that on the basis of present technology the removal of SO_2 from stack gases cannot be justified economically by the recovery of sulfur-containing by-products.

Conclusion

When all has been considered regarding the problem of controlling the undesirable effects of discharging waste or stack gases containing sulfur dioxides into the atmosphere, only a limited number of possible remedies can be listed. This list would include:

(1) The direct approach. This would involve the removal or significant reduction of the sulfur content of medium- and high-sulfur fuels. This is technically possible —within limits—for both fuel oil and coal, but only at appreciably increased cost. Many fuel engineers and coal producers have long argued that the use of cleaned coal at the larger power and utility plants would lead, in the end, to decreased outage and maintenance costs. Lowering of the ash content is of chief consideration in this instance, but reduction of the sulfur content is also a consideration. However, it is generally the practice for these power plants to purchase coal on a basis of direct cost per unit heating value and of minimum freight costs, in the conviction that the equipment can then produce steam at the lowest over-all cost.

Again, for economic and logistic reasons, legal restriction of sulfur contents could not be the answer for the country as a whole.

(2) More efficient dispersion of effluent gases into the atmosphere. High stacks have helped in this regard, but there is a practical limit to the height of stacks, and the topographical and meteorological conditions at some locations are such that increasing the stack height to any practical degree would not help the situation under adverse conditions.

(3) The addition of chemical materials to the fuel to fix the sulfur in solid form. This has been suggested from time to time, but no practical result is known to have been achieved. Inorganic materials have been added to the fuel or in the furnace to assist in the control of boiler deposits and external tube corrosion, but the fixation of sulfur has not been accomplished to a practical degree.

(4) There is, finally, the possibility of washing or treating the stack gases to remove the sulfur oxides before the gases are discharged to the atmosphere, as discussed in some detail in the preceding paragraphs.

The final conclusion must be that none of the methods represent a final practical and economic answer to the nationwide problem of controlling

sulfur emissions from stack gases. Any of the suggested solutions will add an increment of cost to the final cost of the steam generated or the electrical power produced. In the final analysis, whatever the solution, the costs of eliminating or minimizing the effect of the sulfur oxides in stack gases would be passed on to the consumer. If the public demands a solution to the problem, they must do so with realization that higher costs are involved and that additional costs will be passed on to them.

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The Variation of Effluent Concentrations During Temperature Inversions*†

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The study of stack gas dispersion in stable atmospheric conditions is difficult, since the effluent remains aloft for great distances. For many applications, the problem need not be studied as intensively as the more vigorous daytime conditions for this same reason, but growing interest in radioactive aerosols is demanding study of all types of dispersion conditions. One of the reasons for this is that gamma radiation may reach the ground even though the cloud remains aloft. Another is that it is often important to define the effluent behavior hundreds of miles downwind, because of the hazard associated with minute amounts of certain isotopes. Similar reasoning sometimes applies to industrial plants having very large chemical emissions, for here also the inversion condition may create a problem if the terrain pattern downwind is adverse, or because of the fumigation at the breakup of the condition.

A number of people have recognized the importance of the inversion, and have contributed to our present understanding of it. Sutton[6] included values for diffusion parameters during inversion conditions in his 1947 paper, but these bore little relation to the actual patterns of elevated plumes as they were subsequently studied in greater detail. Davidson[2] made an important contribution in recognizing 2 distinct phases in stack gas diffusion, which he termed *aerodynamic* and *meteorological*. His concern, however, was largely with the initial ascent of stack plumes rather than diffusion. Barad[1] derived a mathematical treatment based essentially on the earlier work of Roberts[4], and he was the first to stress the importance of the initial conditions of release when the subsequent rate of diffusion was slow.

Barad and other members of the Brookhaven meteorological staff are credited with several attempts to obtain concentration measurements aloft in 1949 and 1950, but none of these were successful. The recent development of airborne sampling devices[5] has made a sampling program possible.

The data presented are the first obtained from the airborne samplers, and they are by no means complete in any sense. However, they are very interesting in several respects, and it is considered worthwhile to summarize them completely.

Facilities

The Brookhaven meteorological installation, including the 355 ft., 20-in. diam. stack and smoke generating system, has been described previously, but certain additional details are necessary to provide a complete background for this study. Of particular interest are the characteristics of the effluent emission. The tracer is an oil-fog consisting of droplets with a radius of approximately 0.3 μ. The oil emission rate is variable, but has averaged 35 gal./hr. during the current series of tests. The fog is generated in the base of the stack and is carried upward in a stream of air which is also adjustable, but has been maintained at 6975 ft.^{3}/m. during the period in question. This corresponds to a stack speed of 53 ft./sec. The temperature of the mixture at the top of the stack exceeds the ambient by approximately 10-15° C. at this flow rate.

Sampling

The oil-fog has been measured by 3 different techniques, 2 of which have been described in the paper by Smith[5]. The first method involves the 90° scattering of visible light from the oil droplets as they pass through a darkened chamber. The second and third methods both rely on the collection efficiency of the Millipore filter, and the determination of oil amounts is made either gravimetrically or fluorometrically. None of these methods can be used over the entire range of concentrations found in field tests. The calibration of the photometric densitometer breaks down, for example, in the dense plume very close to the stack, and the gravimetric system is ineffective when very small amounts of oil are collected. At any given concentration, it is always possible to obtain comparisons between at least 2 of the methods, and adjustments of concentration and sampling time in the calibration room show the relations of all 3 over part of the range. Table I contains some of the comparisons that have been made. These data were obtained in both the calibration room and at the stack outlet. The results are not ideal, of course, but an agreement within a factor of 2 is quite acceptable for processes dependent on such different physical principles. It will be noted that the fluorometric technique appears to give excessive readings as the oil amount increases. This reflects an extension of the original calibration curve into regions generally far above those that have actually been used, and recalibration is needed to correct this.

Unfortunately, errors do not end with the limits suggested by Table I. The flow rates of the airborne samplers can be measured before and after each operation, but the speed of the pumps aloft is certainly not constant. Most difficult of all is the estimation of the statistical meaning of the samples in reference to theoretical values that can be calculated. In order to appreciate this fully, it is necessary to visualize the technique in some detail. The semi-diesel samplers are carried aloft by Kytoons to the

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TABLE I

Comparison of Various Oil-Fog Measurements

	Method / Filter	mg. of Oil		
		Gravimetric	Fluorometric	Densitometer
CALIBRATION ROOM	1	1.4	1.9	2.4
	2	1.4	1.7	2.4
	3	1.3	1.3	2.0
	4	1.1	1.6	2.0
	5	0.8	0.7	0.7
	6	1.0	0.6	0.7
	7	0.2	0.2	0.3
	8	0.2	0.3	0.3
	9	4.6	7.9	7.2
	10	5.2	9.8	7.2
TOWER				Calculated
	1	8.3	16.6	10.8
	2	6.4	16.5	10.8
	6	3.8	11.8	6.8

Gravimetric—Filter weighed before and after collection.
Fluorometric—Oil extracted with benzol and detected with fluorometer.
Densitometer—Computed from concentration in room as indicated by photoelectric device.
Calculated—Derived from measurements of generator consumption, stack and filter flow.

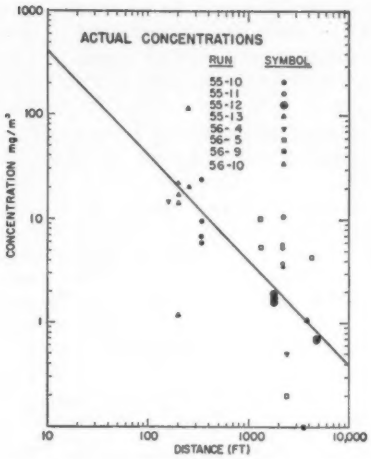

Fig. 1. Actual Concentrations. The original, uncorrected concentration data are shown. Only samples known to be defective have been eliminated.

level of the oil-fog plume. Ideally, each sampler should be held at fixed location in reference to the source, but this is virtually impossible with a Kytoon which moves about with the wind. The only reference of any practical value is the effluent plume itself, and an attempt is made to keep the assembly as near the centerline of the meandering plume as possible. This too can be quite a difficult feat, but at least the proportion of time in which the assembly is improperly located can be judged. These errors, together with smaller ones arising from other sources, reduce the overall reliability of any given sample to approximately a factor of 3. While disappointing in some respects, data of this quality are perfectly suitable for first approximations of stable diffusion.

Analysis

The 2 filter techniques have been used to obtain all of the samples during inversions, and the fluorometric measurements from the first 8 field tests have been carefully examined and summarized for this study. A number were rejected because of known mistakes or defective equipment, but all others are included in this analysis despite the fact that several are probably quite inaccurate. Table II shows the individual samples, as well as other pertinent information. The data are arranged approximately in order of increasing wind speed. The column headed *computed concentrations* represents the plume concentration as determined from the measured oil amount on each filter and the air flow of the individual sampler. Despite the limitations in technique described in the preceding section, the samples are subsequently treated as though they were plume centerline values.

The results begin to be somewhat more meaningful when the field concentrations are plotted against distance, as in Fig. 1. Here, although the scatter of the data is large, one can perceive an orderly decrease in concentration with distance and even fit a line representing the slope fairly easily. This line is in relatively good agreement with the individual slopes in specific tests having samples at 2 or more distances. Tests 55-12, 56-4 and 56-10 are the best examples.

Without making any commitment to a particular theoretical approach, it is worthwhile to inquire what mathematical model might describe this inversion plume. The Sutton equation for a point source at the height of the stack in the free atmosphere is one possibility:

$$\chi = \frac{Q}{\pi C_y C_z \bar{u} x^{2-n}} exp\left[\frac{1}{x^{2-n}}\left(\frac{y^2}{C^2_y} + \frac{z^2}{C^2_z}\right)\right] \qquad (1)$$

For the current study, with all data assumed to be along the centerline $y = z = 0$, the formula reduces to:

$$\chi = \frac{Q}{\pi C_y C_z \bar{u} x^{2-n}} \qquad (2)$$

where:

χ	= concentration	
Q	= rate of pollutant emission	
C_y, C_z	= crosswind and vertical diffusion parameters	m. g.
n	= dimensionless index	sec. units
$\bar{u}$	= wind speed	

Since most theoretical models would suggest that the downwind concentrations would be directly proportional to the rate of emission (Q) and inversely proportional to the wind speed ($\bar{u}$), the concentration data can be simplified by adjusting all values to a standard output rate of 35 gal./hr. and a wind speed of 10 mph. In this survey, Q and $\bar{u}$ are measured, and the normalized concentration figures are shown in the final column of Table II. They are also plotted as a function of distance in Fig. 2. It is immediately evident that the scatter is significantly reduced, and that a line of best fit, determined by eye, is more meaningful. From this line, a value of n can be specified. The most interesting feature of Fig. 2 is that this value of n is approximately 1.00, representing a linear decrease in concentration with distance. This figure for n is much larger than any of which the authors are aware, and suggests that the diffusion process is occurring at

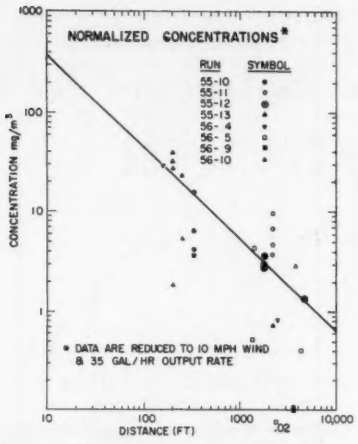

Fig. 2. Normalized Concentrations. The same data as that shown in Fig. 1, adjusted to a standard emission of 35 gal./hr. and 10 mph. wind.

a slower rate than might be expected from most calculations that are currently made. Values of n suggested by others for inversion conditions have normally ranged from 0.30 to 0.50. Barad and Roberts have suggested similar slopes, but with somewhat different mathematical treatments.

Fig. 3 is a plot of several theoretical curves together with a repetition of the line representing the mean of the data. All plots have been extended to the graph boundaries, although it must be remembered that the actual data were all taken within the first mile. The curve designated *Sutton 1947* is equation (2) with $n = 0.4$ and $C_y \times C_z = 0.02$. The *BNL* curve is derived from the same equation, but in this case, $n = 1.0$, $C_z = 0.025$ and $C_y = 0.40$. The *Barad 1951* curve is adapted from his 1951 publication. It is apparent that the *BNL* and *Barad* plots have the correct slope to match that of the actual data, while the Sutton line shows too rapid a decrease. All 3, however, overestimate the observed concentrations by factors ranging from 10 to more than 100 within the first mile.

No inaccuracy in the measurements can account for discrepancies of this

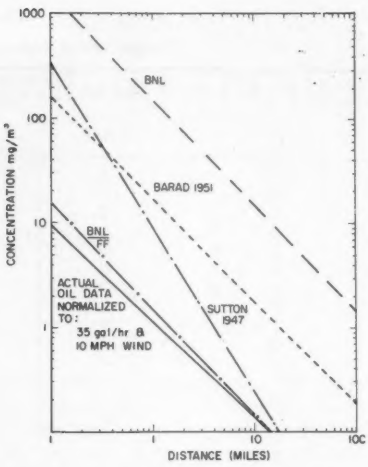

Fig. 3. Plots of Centerline Concentrations According to Diffusion Equations. Three of the 5 plots represent the uncorrected predictions of diffusion equations. The $\frac{BNL}{FF}$ curve is the only one to agree closely with the actual data, and it has been adjusted to do so.

order. The solution is found in the fact that the stack concentration is finite rather than infinite as required by the point source approximation, and in the neglect of the rapid, aerodynamic diffusion which occurs immediately after release of the effluent from the stack. Apparently, very rapid mixing is present for a short time, and then gives way to a more gradual process. This physical explanation is almost a requirement to account for the situation shown in Fig. 3. This is not a new and startling concept. It was a key point in Barad's paper, and the criticism of his work is only that he did not carry his adjustment far enough. He believed that the initial phase was essentially complete about 5 meters from the stack, and that the dilution from this process was about a factor of 5.

This brings up an important problem in terms of mathematical approximations and their application to practical situations. If such large errors can be made in applying a point source formula to the small Brookhaven test stack, it is conceivable that much more serious discrepancies may be found with the high stack speeds and temperatures of large industrial plants.

There are several ways of compensating mathematically for the initial or aerodynamic dispersion. The sim-

TABLE II

Airborne Sampling Summary

Smoke run number	Stack concentration $\chi_s \times 10^4$ mg./m.³	Rate of emission gal./hr.	Wind $\bar{u}$ speed mph.	Distance from source ft.	Time in smoke min.	Computed concentrations from filters χ_f mg./m.³	* $\chi_f \times \frac{\bar{u}}{10} \times \frac{35}{\text{R. of Em.}}$ mg./m.³
56-5	1.1	37.4	1.0	4200	14	4.3	0.40
	1.1	36.6	1.0	1310	6	5.3	0.51
	1.1	36.2	1.0	2380	7	0.2	0.02
	1.1	36.2	4.5	1310	12	10.0	4.26
55-13	0.8	27.4	2.0	250	24	20.6	5.26
	1.0	34.9	2.0	250	18	111.7	22.39
	1.1	36.1	2.0	2210	26	3.7	0.72
55-10	1.0	34.9	6.5	330	3	9.6	6.26
	1.1	36.0	6.5	330	25	24.0	15.2
	1.1	37.3	6.5	330	3	6.8	4.15
	1.1	37.7	6.5	330	11	6.0	3.62
55-11	0.8	27.6	9.0	2210	4	5.8	6.62
	0.9	31.3	9.0	2210	4	3.7	3.72
	1.0	34.9	9.0	2210	24	10.6	9.56
	1.1	36.1	9.0	2210	13	5.3	4.62
56-9	1.2	40.4	11.0	3610	7	0.1	0.10
	1.2	39.8	12.5	3610	35	0.1	0.11
55-12	1.0	35.1	19.0	1800	41	1.9	3.6
	1.1	38.5	19.0	1800	29	1.6	2.77
	1.1	38.5	19.0	1800	22	1.7	2.94
	1.1	36.3	19.0	4920	24	0.7	1.32
56-4	1.0	32.6	19.0	2460	11	0.4	0.82
	1.1	36.2	19.0	160	10	15.0	28.4
56-10	1.4	46.6	21.0	200	16	1.2	1.89
	1.2	41.4	21.0	200	26	17.6	31.3
	1.3	45.1	22.0	200	23	22.8	38.9
	1.2	41.4	22.0	200	23	14.9	27.85
	1.2	39.4	28.0	3780	3	1.1	2.87

*Normalized to 10 mph. and 35 gals./hr.

plest is division of a formula having the correct slope by an appropriate constant. This has been done for the *BNL* equation and is shown in Fig. 3 as the $\frac{BNL}{FF}$ curve. FF, which may be freely translated as *fudge factor*, equals 100 in this study. A second approach would be to use a fictitious point source far upwind of the actual source position, as has been done for pollutant clouds by Holland[3]. This is equivalent to moving the *BNL* curve in Fig. 3 to the left 15 miles, instead of lowering it by division. Barad's method is more accurate in representing the actual physical behavior, since he treats the problem in 2 steps.

Each of these methods can produce correct predictions of the centerline concentrations over short distances, and presumably over much longer ones *if* the natural diffusion parameters remain nearly constant. The important point is that each requires knowledge of the initial dilution of the cloud before the proper adjustment can be made.

Another solution lies in the use of an equation of the Sutton form with values of the parameters, particularly *n*, adjusted to match the actual data at distances of interest. This also implies some knowledge of the field concentrations, and it is much less appealing in that it can fit the facts only at one distance. The original Sutton curve shown in Fig. 3, for example, would give good results at a distance of 10 to 25 miles, but would always be in error at other points. Close to the stack, the equation would overestimate the concentrations, and at distances greater than 50 miles, the underestimation would become serious.

No mention has been made of the vertical and crosswind diffusion, represented by the parameters C_z and C_y in equation 2. This is because the centerline concentration data provided by this sampling technique do not reveal anything about them individually. These parameters appear in the denominator of the equation, as does the FF factor used to correct the predicted values, and it is legitimate to suggest that a large portion of the discrepancy might result from choices of C_z and C_y. Fortunately, they are related to the vertical and horizontal spread of the cloud as well as the centerline concentrations, and some reasonable conclusions about their magnitude can be drawn from photographic and visual observations. Specifically, the width and vertical thickness of the trail can be used to establish maximum limits for both parameters. For the Brookhaven plume, it is difficult to see how the values could exceed 0.05 for C_z and 0.50 for C_y. Actually, it is felt that 0.025 and 0.40 are closer to the truth. Therefore, the correction factor, however it is achieved, must reduce the concentration by approximately a factor of 100.

One obvious point should be discussed, and that is the relation between diffusion and the steepness of the inversion. Unfortunately, these data cover too small a range of conditions to define any specific relationship. Summaries of many visual observations from previous runs suggest, however, that the important differentiation is between lapse and inversion, and that the influence of the degree of temperature increase with height is secondary.

Conclusions

The first set of inversion concentration data obtained at Brookhaven from the 355 ft. test stack facility have been presented and analyzed. The data, though scanty, reveal that diffusion within the first mile from the source agrees with the pattern suggested by Barad, in which an initial aerodynamic diffusion process is followed by a very gradual, natural one. However, it is somewhat surprising to find that the initial diffusion is much more rapid than had been anticipated, and also that the subsequent natural process is more gradual.

Accurate prediction of the inversion diffusion concentrations is made difficult by the marked, 2-stage nature of the plume behavior. Little enough is known of the natural rates of diffusion, but even if that process could be described precisely, errors amounting to factors of 10 to 1000 may be introduced by neglect of the initial dilution. Discrepancies of this order are too large to be acceptable for many purposes, and careful investigation of effluent plumes close to the stack is a prerequisite to improvement of the estimates.

Acknowledgments

Many others of the Meteorology Group staff have assisted materially in the development and conduct of the inversion sampling program. Chief among these are Robert M. Brown, Gilbert S. Raynor and George Potts. Isaac Van der Hoven and Gerard DeMarrais of the U. S. Weather Bureau Office located at the Laboratory have also participated in the field work.

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Atmospheric Dispersal of Industrial Stack Gases Determined by Concentration Measurements In Scale Model Wind Tunnel Experiments*

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The value of scale model experiments in the investigation of various physical phenomena is sometimes limited by the form of data obtained. If the experiments have a high degree of similarity to the prototype phenomena, then the more quantitative the nature of the data, the greater will be the usefulness of the results. Measurement of degree of similarity between a scale model and the prototype would be improved by quantitative data on which to base a correlation. Whether a high degree of refinement in the data-taking phase of an experiment is necessary or desirable depends on many factors, not the least of which is cost. Quantitative forms of data require more elaborate instrumentation and in addition usually require a closer control of experimental conditions. Various supplementary apparatus may also be needed. The time required to conduct the experiments as well as to set them up may be increased considerably.

Visual and Optical Techniques in Wind Tunnel Experiments

Scale model wind tunnel experiments on air pollution have been performed with various methods of data detection. Perhaps among the earliest were those in which geometric features of the smoke plume were observed or recorded photographically. This continues to be an effective means of obtaining important plume characteristics. In addition to obtaining certain plume details it gives an excellent overall view of smoke dispersal and associated air motions. This technique does not provide data of the form most effective for correlation with full scale ground level gas concentration experiments. It does, however, show the relative effect of building and stack modification on displacement and dispersal of smoke or gas plumes.

In an attempt to improve on the visual and photographic methods a refinement was developed at the New York University 3½ by 7 ft. Wind Tunnel to remove some of the human element in gauging smoke plume characteristics[1, 2]. The presence or absence of smoke—usually at ground level—was detected by the interruption of light in a beam projected across the airstream and directed at a phototube. Reduction in phototube output was an indication of the presence of the smoke plume at the level of the light beam. Graphs of change in phototube output vs. wind speed were used to determine the wind speed at which the smoke plume first caused pollution. This gave the dividing point between pollution and no pollution on the wind speed scale. Used in conjunction with climatological data this provided the information for calculation of annual hours of pollution. Data on wind speed at which pollution first occurs is of value in correlation with full scale field studies. Field measurements of gas concentrations may be used for finding this same characteristic. A correlation of this type is shown in reference 1 where excellent agreement of wind tunnel and field studies was found.

Data obtained from the light beam-phototube method is a measure of smoke concentration. It is, however, a line concentration which is not the form usually desired. In an idealized situation, line concentration is proportional to point concentration but the units are different. As experience was gained with the light beam-phototube method in the New York University wind tunnel there developed a tendency to look at phototube data in terms of their significance as potential concentration measurements. The need for concentration data was brought out in connection with one investigation in which a stack modification applied to full scale resulted in what appeared to be a greater improvement in pollution characteristics than indicated in the wind tunnel experiments. It was found in later investigations that modifications which increase the wind speed of initial contact of plume with ground also reduce the concentration at higher speeds.

The possibility of developing the light-beam technique into a point concentration type was studied. There were instruments available on the market for smoke concentration measurement and there appeared to be sufficient reasons for putting effort into developing the necessary equipment and techniques. One of the potential difficulties important in the decision to develop the gas tracer technique described below was the problem of controlling and keeping constant the density of smoke supply. There is also the need for a separate instrument for monitoring of smoke concentration in the model stacks.

The availability of instruments suitable for measurement of sulfur dioxide concentrations at low levels led to the development of techniques and equipment currently in use at the New York University wind tunnel. Sulfur dioxide concentrations of less than 1% in the stack air supply are sufficient to give measurable concentration in the plume. The relative ease of measuring sulfur dioxide flow rate together with negligible toxicity problems due to small amounts of sulfur dioxide involved made this procedure quite appealing.

Various auxiliary equipment was needed as the result of using gas concentration techniques. The stack gas supply system became more complicated. Increased attention was needed in regard to leaks. The prob-

* Presented at the 50th Annual Meeting of the Air Pollution Control Association held in St. Louis, Mo., June 2-6, 1957.

lems of corrosion of materials by sulfur dioxide and absorption of sulfur dioxide by pipes and tubing arose. In contrast with the photographic technique of obtaining measurement of the entire smoke plume in one record, the gas concentration technique requires measurement at a number of individual locations. An apparatus was necessary for moving the sampling probe from point to point to obtain maximum effectiveness. The various developmental problems have been largely solved and successful operation has been achieved.

Scale Factors

The importance of Froudes number in experiments which involve gas density effects was pointed out in references 1 and 2. In addition to Froudes number, density ratio (stack gas to ambient air) and geometric similarity are to be maintained at the same values for model and prototype. These lead to the following relationships for model test variable in terms of their full scale counterparts.

$$V_m = V_f \sqrt{l_m/l_f}$$
$$(V_s/V)_m = (V_s/V)_f$$
$$(\rho_s/\rho)_m = (\rho_s/\rho)_f$$

where

V = wind speed
V_s = stack gas ejection speed
ρ = ambient air density
ρ_s = stack gas density
l_m/l_f = linear scale factor

and subscripts m and f refer to model and full scale, respectively. In the absence of special controls and unnatural effects, the wind tunnel airstream includes no thermal effects in the form of convective turbulence. This is the same neutral or adiabatic condition that would be approached at the higher wind speeds of the atmosphere.

Concentration Measuring Apparatus and Technique in Wind Tunnel Experiments

In order to evaluate the pollution characteristics of exhaust gases under various test conditions, as simulated in the 3½ by 7 ft. Wind Tunnel, controlled volumes of a tracer gas were introduced into the effluent. There was an available instrument specifically designed to continuously record the concentration of oxidizable sulfur compounds in a gas stream. Of the possible compounds, sulfur dioxide was chosen because of its availability and convenience. Also it has some psychological advantage in that sulfur dioxide is frequently the pollutant under investigation in the full scale case.

The instrument used is a Consolidated Electrodynamic Corp. Titrilog (model 26-103) which has been slightly modified to facilitate its use in tunnel tests. Briefly, the principle of operation of the Titrilog is one of an oxidation-reduction reaction in conjunction with an electronic amplifying system. A continuous sample containing oxidizable sulfur compounds is drawn either under pressure or from slightly below atmospheric pressure into a titration cell where it is titrated with electrolytically generated bromine at a potentiometric balance point. A feed-back amplifier controls the rate of generation of the reacting bromine above a set reference level so that it is at all times equal to the rate of absorption of reactive gas in the titration cell. The current through the amplifier system is measured continuously by a recording milliammeter. The difference between the current during the reaction period and during the zero level period is a function of the sulfur compound concentration in the incoming sample gas. Since what is recorded is the net titration level, actual concentrations are obtained by multiplying this value by a calibration factor which is determined separately for sulfur dioxide or any other constituents to be measured.

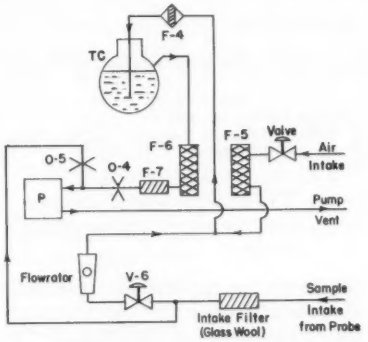

Fig. 1. Modified gas handling system for titrilog instrument.

F-4 Dust Filter, Cell
F-5 Air Charcoal Filter
F-6 Pump Charcoal Filter
F-7 Pipe Cleaner Filter, Pump Orifice
O-4 Pump Orifice
O-5 Bleeder Orifice
P Vacuum Pump
TC Titrilog Cell
V-6 Sensitivity Valve

The method of calibration used at the wind tunnel is basically as follows. Controlled volumes of air and sulfur dioxide are thoroughly mixed to produce a stream of gas containing a known concentration of sulfur dioxide which is then ducted through a manifold system. At some point downstream, a probe has been inserted in the center of the gas stream and samples of the mixture are continuously drawn off and fed to the Titrilog. The net titration level determined from the recorder is divided by the sample rate and plotted as a function of the known concentration to produce a calibration curve for sulfur dioxide.

The Titrilog (model 26-103) has been modified to suit the requirements of the tunnel operation (Gas Handling System — Fig. 1). Since the tests require maximum sensitivity, the pressure system has been removed and the vacuum system used exclusively to draw a continuous sample of tunnel air. The sample rate is determined by the critical flow orifice. When pure sample is drawn the rate is approximately 900 cc./min., allowing measurement of a range of sulfur dioxide concentrations of about 0-7 ppm. To increase the range a controlled volume of filtered air can be introduced to the sample line. Since the total flow is fixed by the critical orifice the rate of gas sample drawn from the tunnel is thereby reduced. The sample rate can be determined at any given time since the polluted gas sample is passed through a flowrator before reaching the titration cell and before the point at which the filtered air is introduced.

At the present time, the Titrilog is situated outside of the tunnel test section while the intake probe is inside the tunnel, mounted well upwind of the supporting carriage unit, which is designed to allow the probe to be remotely positioned to any desired point in the tunnel test section with a minimum of disturbance to the flow patterns. A long length of flexible chemical resistant plastic tubing is used to carry the sample from the probe to a feed-through tube in the tunnel wall to the Titrilog. To decrease the time required for a given sample to get from the probe to the Titrilog, a tee has been inserted in the intake line before the sensitivity valve. At this tee, a connection is made with the pump bleeder orifice,

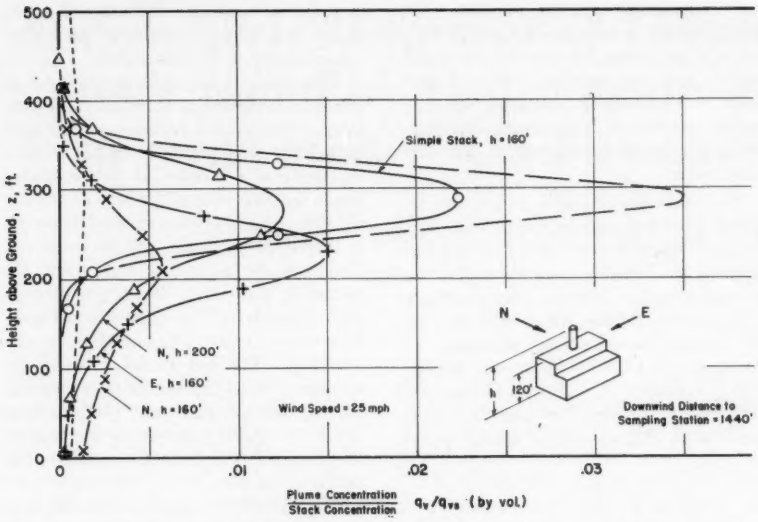

Fig. 2. Vertical concentration profiles through plume 1440 ft. downwind of stack for various configurations.

——— Wind tunnel experiments — Model Scale: 1" = 20'.
— — — — Sutton parameters } Sutton diffusion equation using Plume
- - - - - - - - - - - - Smith & Singer parameters { Height of 288'.

thereby increasing the vacuum and drawing a greater sample in a shorter period of time. The excess sample not passing to the titration cell is passed directly to the vacuum pump for exhaust.

In order to further shorten the intake lines and, as a result, decrease the reaction time, it is planned to mount the entire Titrilog on the carriage inside of the tunnel. At that time, the sensitivity valve and air valve will each be by-passed by a system of orificed solenoid valves. By proper selection of orificed sample and filtered air solenoid valves, predetermined sample ratio can be established and controlled remotely from outside of the tunnel test section.

To study the distribution of sulfur dioxide resulting from stack gases, the wind tunnel provides for control of the following variables:

(1) Building design
(2) Stack design (including height and diam. and nozzles)
(3) Density of effluent (through the use of a mixture of air and helium or by the use of individual heater units)
(4) Total effluent gas flow vol.
(5) Initial sulfur dioxide concentration
(6) Wind speed
(7) Wind direction (rotation of model)
(8) Three dimensional remote positioning of the sampling probe

(Downwind range depends upon scale of model. At 30 ft. = 1 in. the maximum range is about 10,500 scale ft.). The data collected and presented in this report is the result of maintaining constant effluent density, total gas flow volume, initial sulfur dioxide concentration and wind speed. The primary variables in all the tests were the downwind, vertical and horizontal positions of the sample probe. Other tests involved changes in stack design, wind direction and the addition of a building.

When the Titrilog is drawing maximum sample from the tunnel (870-900 cc./min.) each division of the record corresponds to approximately 0.20 ppm. by volume. Good estimates of values can generally be made as low as 0.05 ppm. by volume and on some occasions as low as 0.025 ppm. by volume, depending on the stability of the instrument's zero reading. It is operational practice to use as the zero level that reading which is obtained from the sample drawn from the tunnel stream without sulfur dioxide being emitted from the stacks. It is generally noted that this zero level is slightly higher than that determined from the pure filtered air supply of the instrument. It is also operational procedure to read an average value of the recorder trace as the concentration measurement for each test condition. In this manner variations due to slight variations of tunnel wind speeds and initial sulfur dioxide concentration *etc.* are, to a large extent, screened out.

Experimental Results

Results of experiments on a simple scale model with one stack are shown

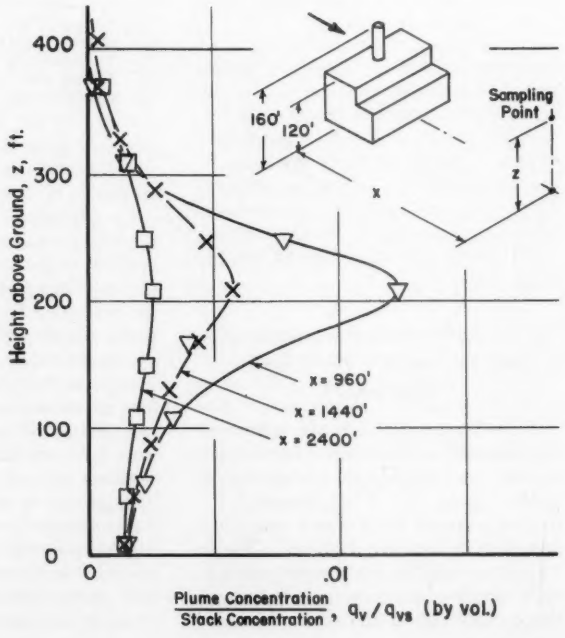

Fig. 3. Vertical Concentration Profiles at Various Distances Downwide of Stack.

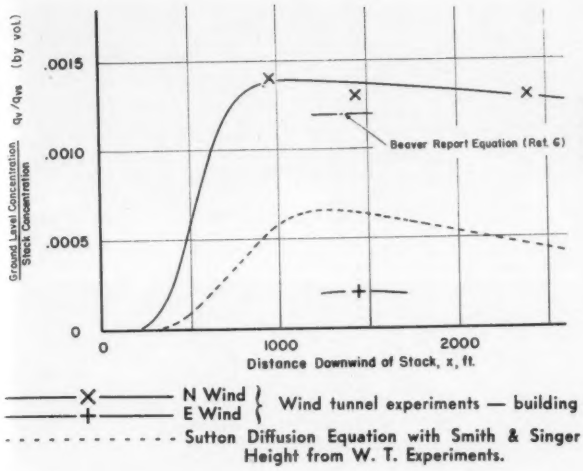

Fig. 4. Ground Level Concentration vs Distance Downwind of Stack.

in Fig. 2, 3 and 4. The various essential data are as follows:

Prototype characteristics:

Stack diam. (internal)
$d_s = 13.75$ ft.

Stack height variable

Stack gas ejection speed,
$V_s = 72$ ft./sec.

Stack gas temperature,
$t_s = 150°F.$

Ambient air temperature,
$t = 70°F.$

Wind speed,
$V = 25$ mph.

Model characteristics:

Linear scale, 1/240 (1 in. = 20 ft.)

Velocity scale, 1/15.5

Stack effluent — mixture of helium and air with density which gives same density ratio of effluent to ambient air as in prototype.

SO_2 in stack effluent — 3000 ppm. (ppm. by vol.)

All results are expressed in terms of full scale equivalents.

The results of SO_2 concentration measurements are expressed as a ratio of concentration at sampling point to concentration in stack, q_v/q_{vs}, by vol. Variables involving stack gas density are calculated on the basis that the prototype effluent has the same molecular weight as air. Its density in relation to ambient air is, therefore, determined solely by its temperature.

Other than the model there were no obstructions to air flow in the wind tunnel airstream. The airstream passed over a smooth floor (with some surface imperfections) for a distance of approximately 18 ft. before reaching the model. The model of the building was 6 in. high and 15 in. long. The test section airstream is rectangular in shape: 3½ ft. high and 7 ft. wide.

Results obtained with the building tested in these experiments must be viewed as only one case of building configuration, stack effluent characteristics, and wind speed. While certain generalizations may be made, various details of results are not necessarily representative of other situations. It is hoped that these data will be viewed as an example of a technique in scale model experimentation.

Comparison of concentration profiles of the plume from the simple stack with those having the building present show 2 general effects of building interference. In Fig. 2 (results for downwind distance of 1440 ft.), the height of the plume without the building is 288 ft. (defined as the height of the peak concentration). With the building present, plume heights are 210 ft. with a north wind and 230 ft. with an east wind, both lower than the simple stack plume. Another effect is evident from inspection of the vertical concentration profiles. In contrast with the profile of the simple stacks, those with the

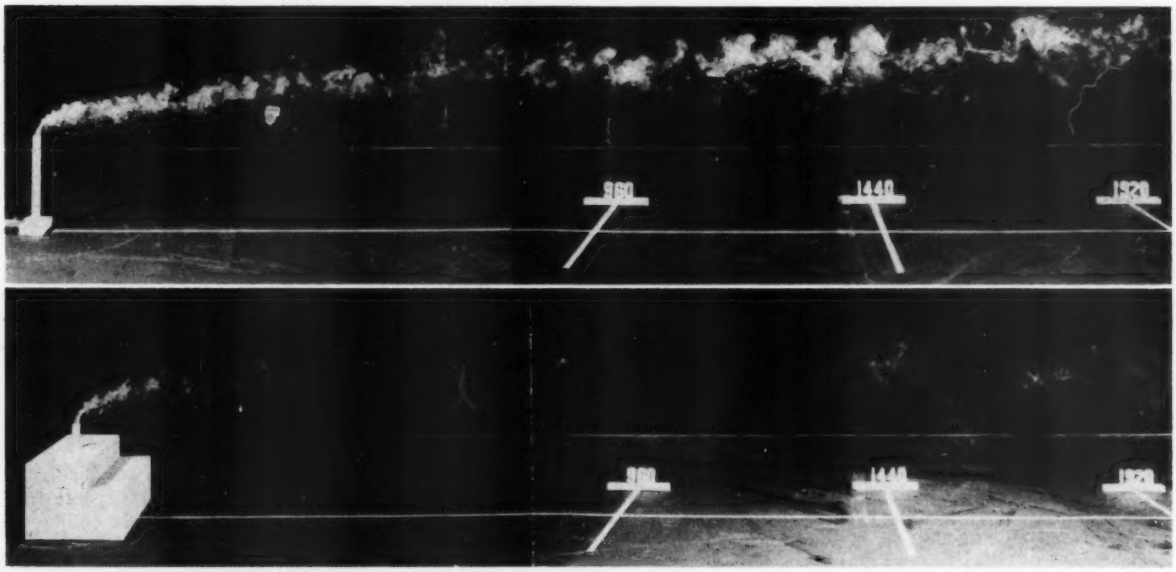

Fig. 5. Effect of configuration (160 ft. stack). Upper figure—simple stack. Lower figure—roof based stack.

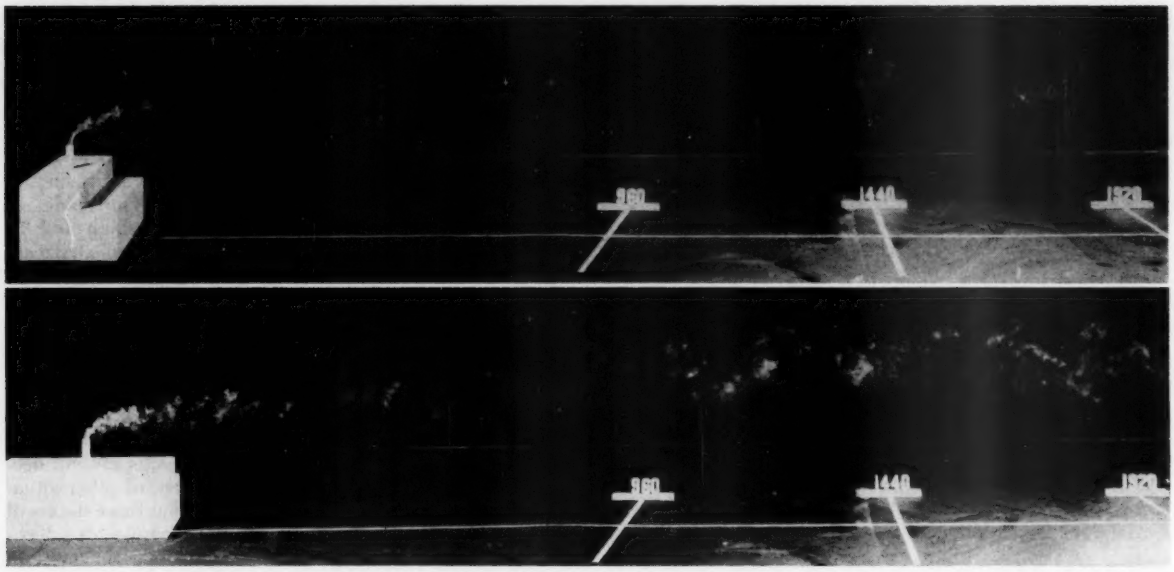

Fig. 6. Effect of building orientation (160 ft. stack). Upper figure—long axis perpendicular to wind (north wind). Lower figure—long axis parallel to wind (east wind).

building present showed a decided asymmetry. The concentrations in the regions below the peak are greater than those above. This may be due to the greater turbulence near the ground caused by the building. The plume disperses more rapidly downward than upward. Lowering of the plume and greater downward dispersion both tend to increase ground level concentration.

The marked effect of wind direction is evident in comparing the results for north and east winds. The north wind is much less favorable for ground level concentration although the reverse is the case for peak concentration. For north winds the building presents its longest dimension normal to the airstream, and causes more turbulence and distortion of air flow. Increase in stack height moves the plume away from the turbulent region and is favorable to reducing ground level concentration. The increase of 40 ft. in stack height between the 2 cases tested resulted in an increase of approximately 65 ft. in plume height. Ground level concentration for the 200 ft. stack was about $\frac{1}{6}$ of the value for the 160 ft. stack. Theory for a simple plume (no building interference) would show this ratio to be about $\frac{2}{3}$. The effectiveness of stack height when the plume is dominated by building turbulence is brought out in these experiments.

The effect of downwind distance is shown in Fig. 3 and 4. The expected decrease in peak concentration is shown in Fig. 3. It is to be noted that the plume height remained approximately 210 ft. for the 3 distances tested.

The simple stack plume continued to rise over this distance. At 1440 ft. (test condition of Fig. 2) its elevation was 288 ft. while at 960 ft. and 2400 ft. it was approximately 254 ft. and 358 ft., respectively. It must be emphasized other wind speeds would show a considerably different result. Ground level concentrations with the building present vary only slightly with distance in range tested beyond 1000 ft. The relatively flat curve of ground level concentration over a considerable distance (beyond the initial low values close to the source) seems typical of situations with a high degree of building turbulence.

It is interesting to compare the results of these experiments with some predictions of theoretical and empirical analyses. These cannot be viewed as direct comparison since some of the physical conditions are quite dissimilar. Plume path equations of Bosanquet, Carey and Halton (summarized in ref. 7) show plume heights somewhat lower than the wind tunnel result for the simple stack.

Gas concentration profiles for a simple plume calculated with Sutton's diffusion equation are shown in Fig. 2. Height of plume found in the experiment were used in these calculations where needed. One profile results from using the diffusion parameters of Sutton for zero temperature gradient and 100 m. height (tabulated in ref. 7, p. 53). The other profile results from parameters found in Brookhaven field studies by Smith and Singer (ref. 5) for B, gustiness type. Sutton's parameters are considered to be representative of 3 min. sampling periods while those of Smith and Singer are based on hourly means. Since wind tunnel experiments do not include long period fluctuations of air motion, it is believed they are representative of shorter sampling periods.

Theoretical ground level concentrations vs downwind distance are shown in Fig. 4 for Smith and Singer parameters. Sutton's parameters yield negligible ground level values. Maximum ground level concentration calculated by the equation in the *Beaver* report (ref. 6, p. 52) is shown. In the reference it is stated that the maximum occurs about 25 to 35 times the height of stack. This location is beyond the range shown in Fig. 4.

Conclusion

Wind tunnel scale model experiments are more useful when performed with sulfur dioxide concentration equipment. In application to air pollution problems of industrial plants the effects of plant configuration and stack parameters can be evaluated more effectively. Since tolerance of air pollutants is often ex-

pressed in terms of concentration values, direct measurement of concentrations in model experiments gives a more meaningful result.

Correlation of wind tunnel experiments with field studies will be more significant with this quantitative form of data. Increased use and confidence in scale model experiments will depend on significant correlation studies.

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Atmospheric Dispersal of Industrial Stack Gases Determined by Concentration Measurements In Scale Model Wind Tunnel Experiments - - A Written Discussion

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We have reviewed the subject paper with considerable interest, both because it is one of the few instances in which quantitative concentration data have been obtained in wind tunnels and because comparisons are made with field results which we have obtained at Brookhaven. Unfortunately we feel that we must take issue with two points in the paper.

The general criticism we have to offer concerns the normalization of the downwind concentration data by the stack concentration, and the comparison of these values with the calculated concentrations predicted by the point source formula presented by Sutton. We feel that this procedure, as illustrated in Fig. 4, is arbitrary and misleading in that it suggests that the downwind concentrations are dependent upon the stack concentration, whereas in the Sutton formula they are dependent upon the rate of emission. The authors do not enlighten us on this point, but if the tunnel tests are actually dependent primarily on the stack concentration rather than the rate of emission, the fit between the curves in Fig. 4 is arbitrary. A simple adjustment of the air flow in the stack while holding the rate of emission constant will make the fit appear better or worse. If additional data are available, it is felt that the point should be clarified, for the usefulness of the tunnel is more easily evaluated if one knows what mathematical models are satisfied.

We must take vigorous exception to Fig. 2 insofar as it applies to the curve representing Brookhaven parameters. We have calculated the appropriate vertical profiles for the parameters given in the reference paper, and find that the authors have apparently used the values for the B_2 gustiness condition, which was explicitly described in our text as representing *very light winds and a superadiabatic lapse rate*. This is one of the conditions least likely to be simulated in the tunnel, and could hardly be expected to show any resemblance to either the Sutton or tunnel profile as shown. The implication of the figure that the tunnel and Sutton results agree, but those of Brookhaven are markedly different is therefore invalid.

Authors' Closure

G. H. STROM, M. HACKMAND and E. KAPLIN

It was our intention to describe an experimental technique of interest to air pollution investigations and present illustrative results without becoming involved in a discussion of methods of data presentation. Perhaps additional material on conversion of units from those used in Sutton's diffusion formula would be helpful to the reader.

We are not clear on precisely what Messrs. Smith and Singer object to in our method of presentation except possibly a preference for another method. Conversion from the units used in the original form of Sutton's formula to those used in the paper is straightforward. Messrs. Smith and Singer seem to imply that stack concentration and rate of emission are independent but this is not the case unless a special adjustment of other variables is made. As used in the paper, stack concentration is proportional to rate of emission. Adjustment of any variables other than stack concentration will lead to results different from those shown. Also stack concentration must be limited to small values or an additional factor must be included, as shown in the equation below.

The following equation relates volume concentration ratio q_v/q_{vs} with mass concentration χ and emission rate Q_c used in Sutton's formula. The contaminant (SO_2 in this experiment) and the remainder of the stack efflu-

ent (here termed stack gas) are identified separately although mixed physically.

$$\frac{q_v}{q_{vs}} = \frac{\rho_s M_a V_s A_s}{\rho_a M_s (1 + q_{vs})} \cdot \frac{\chi}{Q_c}$$

where:

χ = concentration of contaminant at a given location in plume, mass/unit vol. of air.
Q = emission rate, mass/unit time.
q_v = volume of contaminant/unit vol. of air in plume at location where χ is found.
q_{vs} = volume of contaminant/unit vol. of stack gas in the stack.
ρ = density, mass/unit vol.
M = molecular weight.
V_s = gas ejection speed at stack.
A_s = stack area at exit.

The following subscripts apply to ρ, Q and H.

s = stack gas (excluding contaminant)
c = contaminant
a = atmospheric air

In terms of emission rates.

$$q_{vs} = \frac{Q_c/M_c}{Q_s/M_s}$$

For small values of g_{vs} and equal molecular weights of stack gas and air, the above equation reduces to the following form which was used in calculations for the paper.

$$\frac{q_v}{q_{vs}} = \frac{\rho_s V_s A_s}{\rho_a} \cdot \frac{\chi}{Q_c}$$

The Brookhaven parameter from ref. 5 used in calculation of concentration profiles in Fig. 2 and 4 are for gustiness classification B_1. This designation was inadvertently omitted in the preprint. It may have been better to use C classification parameters as a closer approximation of scale model turbulence conditions in which case the concentration profile would show higher peak values and lower ground level values. We are unable to reconcile the contention of Messrs. Smith and Singer that B_2 parameters were used. One point should perhaps be emphasized though it does not appear to explain the disagreement. The calculations and graphs were made for full scale values of stack dimensions, velocities, *etc.* This assumes that concentration ratio measured at a given location in the model applies directly to the geometrically similar full scale location. If the calculations were made for the model values, there would be a scale effect on diffusion parameters, one which maintains geometry of plume independent of scale.

The Sutton and Brookhaven parameters were used in the calculation of concentration profiles as these appear to cover the range of sampling periods reported in the literature. As pointed out in the paper, it is expected that wind tunnel results would be closer to the shorter sampling periods. There is no reason to believe that the long period and wind tunnel profiles should agree.

The Dispersion of Stack Gases In Stable Atmospheres*†

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Among the many factors which affect the lower atmosphere's capacity to diffuse and transport gaseous and particulate materials, the one most easily recognized is the hydrostatic stability or the density stratification of the lower atmosphere. The descriptive terms *fanning*, *coning*, and *looping* have become a standard part of the vocabulary of workers in this field and are almost automatically associated with stable, neutral, and unstable temperature or density stratifications. These qualitative classifications of diffusion and transport phenomena have proved exceedingly useful in studies of these phenomena, but *quantitative* accounting of the effects of variable density stratification has been a major stumbling block in the specification of the atmosphere's capacity to dilute and remove extraneous materials.

It is of course recognized that the density stratification of the atmosphere can play only an indirect role in the processes of diffusion and transport since these processes must ultimately depend upon the *motions* of the atmosphere. The stability of the atmosphere is of interest only insofar as it exerts limiting controls upon the motions of that atmosphere. The inclusion of the effects of a variable density gradient in the formulation of comprehensive theoretical treatments of turbulent diffusion is an exceedingly complex problem. To quote Sutton[1], . . . *the introduction of a variable density gradient means that the mathematical theory is considerably more complicated than that for a homogeneous fluid, and at the present time hardly exists.*

In addition to this lack of a satisfactory theoretical model which includes the effects of vertical density gradients, there is also at present a dearth of reliable measurements of the diffusion and transport of materials in non-neutral atmospheres. This is particularly true of the case of stable temperature stratifications. Since a knowledge of what must be explained is a prerequisite to any theoretical treatment of this problem, it is natural to attack the experimental problem first. It is the purpose of this paper to report upon attempts to measure the diffusion and transport of materials emitted continuously from an elevated point source into stably stratified atmospheres and, insofar as these data permit, delineate the potential hazards and benefits which may arise from such emissions.

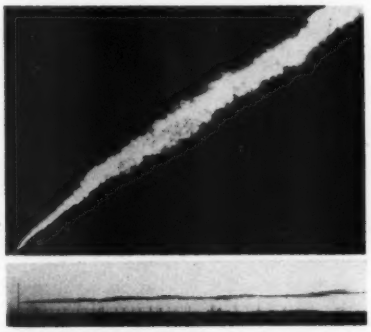

Fig. 1. Aerial and side view of a smoke plume emitted into stable atmospheres showing smoke out to approximately ¾ mile from the source. Source height: 200 ft. above ground level.

The practical importance of a firmer knowledge of the diffusive and transportive capacity of stable atmospheres can be emphasized by the frequency of occurrence of this condition and the fact that in stable atmospheres material may be carried to distant points in relatively high concentrations. The frequency of occurrence of stable atmospheres varies from one locality to another but is generally high. For example, at Hanford the lowest 200 ft. of the atmosphere is characterized by a stable temperature stratification some 40% of the time. Most assuredly this situation must be taken into account in a comprehensive survey of the capacity of the atmosphere to remove and disperse extraneous materials.

Description

An excellent description of the behavior of stack effluents emitted into stable atmospheres has been given by Barad[2]. In the presence of a horizontal wind, an effluent (say, smoke) emitted vertically through the stack orifice is turned from its initial vertical motion and at some height above the stack exit its motion is purely horizontal. From this point on the smoke remains at this height as it moves downstream from the source. Vertical motions on a scale large enough to displace whole segments of the plume are lacking. However, as it moves downstream the smoke spreads in both the horizontal and vertical crosswind directions due to diffusive mixing with the ambient clear air. The horizontal growth of the plume is considerably more pronounced than the vertical growth. In response to larger scale fluctuations of the horizontal wind velocity the plume also meanders about the downwind axis defined by the mean wind direction. The plan and elevation views of a smoke plume emitted into a stable atmosphere shown in Fig. 1 are typical of this situation and illustrate the above description.

In order to establish a model against which measurements of the distribution of effluent concentrations downwind from an elevated source may be appraised, it is assumed that

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† Based in part on a dissertation submitted to the University of Chicago in partial fulfillment of the degree of Doctor of Philosophy in Meteorology.

the following conditions are fulfilled at any distance x along the direction of the mean wind:

(1) When averaged over a considerable period of time, the effluent material is normally distributed about the centerline of the plume with zero mean and variance σ^2_c in the horizontal cross-wind direction and variance σ^2_z in the vertical direction. This distribution is averaged about the *moving* centerline of the plume.

(2) σ^2_c and σ^2_z are independent of the horizontal cross-wind position of the plume centerline and of each other.

(3) The horizontal cross-wind position of the plume is normally distributed about the mean wind direction with zero mean and variance σ^2_N.

(4) The vertical position of the plume centerline is invariant with time or distance from the source.

Under these assumptions, the average distribution of concentration within the plume, X_c, is given by,

$$X_c(x, \eta, z) = \frac{Q}{\sqrt{2\pi}\,\sigma_c\,\sigma_z\,u} exp\left\{-\tfrac{1}{2}\left(\frac{\eta^2}{\sigma^2_c}+\frac{z^2}{\sigma_z{}^2}\right)\right\} \qquad (1)$$

where u is the mean wind speed, Q is the emission rate, and the coordinate system is chosen such that x is along the mean wind direction, y is measured horizontally cross-wind, z vertically, and η is measured along y from the centerline of the plume which is located at (x, Y, o), the origin for y and z being chosen as the centerline of the plume, (Fig. 2). Now, if N is the fraction of time the plume centerline is located between $Y \pm \tfrac{1}{2}$ dy, according to assumption 3

$$N(x, Y) = \frac{1}{\sqrt{2\pi}\,\sigma_N} exp\left\{-\tfrac{1}{2}\frac{Y^2}{\sigma_N{}^2}\right\}. \qquad (2)$$

Then the average concentration observed at the *fixed* point (x, y, z) is given by

$$X_T(x, y, z) = \int_{-\infty}^{\infty} N(x, Y)\, X_c(x, \eta, z)\, d\eta. \qquad (3)$$

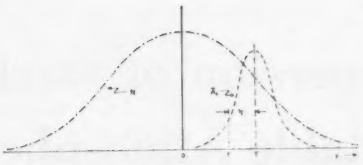


Fig. 2. Assumed cross-wind distribution of concentration within the plume, χ_c, and the center-line position of the plume, N, at a fixed distance.

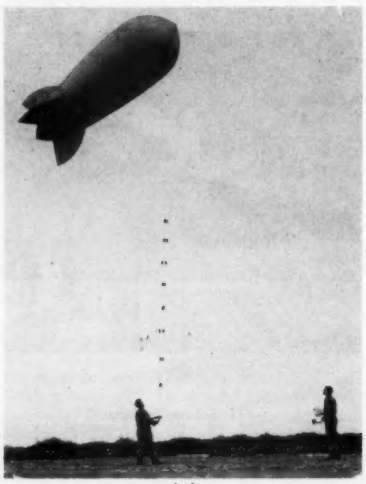
Substituting for N(x, Y) and X_c(x, η, z) from equations *(1)* and *(2)* and recognizing that $Y = y - \eta$, integration of equation *(3)* yields

$$X_T(x, y, z) = \frac{Q}{\sqrt{2\pi}\,\sigma_T\,\sigma_z\,u} exp\left\{-\tfrac{1}{2}\left(\frac{y^2}{\sigma^2_c}+\frac{z^2_T}{\sigma^2_z}\right)\right\} \qquad (4)$$

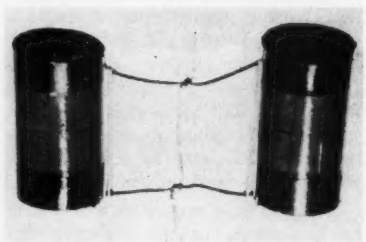
when the continuity requirement

$$Q = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} u\, X_T(x, y, z)\, dz\, dy \qquad (5)$$

is applied and $\sigma^2_T = \sigma^2_N + \sigma^2_c$.



(a)



(b)

Fig. 3. The sampling equipment used to measure the vertical distribution of concentration of fluorescent pigment particles emitted continuously from an elevated point source. (a) Complete assembly; (b) close-up of the impaction sampler.

Equations *(1)* and *(4)* provide the mathematical models which may be used to evaluate experimental measurements. Note that in equation *(4)* the effects of diffusive mixing and of horizontal meandering of the plume on the average concentration measured by a fixed observer are clearly separated. It now remains to determine the dependence of σ^2_N, σ^2_c, and σ^2_z upon the distance from the source and the fluid motions.

The Experimental Measurements

Two rather different techniques have been used by the Atmospheric Physics Operation at Hanford in the determination of the horizontal and vertical variances necessary to an evaluation of equation *(4)*. In order to evaluate σ^2_N and σ^2_c at various distances up to 2000 ft. from the source, aerial photographs of a continuous smoke plume emitted from the 200-ft. level on the Meteorology Tower were taken from an altitude of 6000 ft. directly above the plume at 1-min. intervals for the duration of a steady stable meteorological condition. The aerial view of the smoke plume in Fig. 1 is one of these photographs.

The vertical distribution of a fluorescent pigment emitted continuously from the 185-ft. level was measured by an array of impaction samplers held aloft by a captive blimp. These samplers were kept in the center of the plume at a fixed radial distance from the source. The impaction sampler used and a field assembly of this equipment are shown in Fig. 3.

In the analyses of these measurements the visual width and the horizontal displacement of the centerline of the plume from the downwind axis defined by the mean wind direction were measured at 200-ft. intervals, from the source out to 2000 ft., from each photograph. From these measurements the variance of the horizontal displacement of the centerline was calculated from,

$$\hat{\sigma}^2_N = \frac{1}{m}\sum (Y - \overline{Y})^2 \qquad (6)$$

where the summation extended over m observations of Y and the circumflex indicates an estimated value.

Estimates of the variance of the average distribution of concentration within the plume cannot be derived directly from measurements of the width of the plume but the following

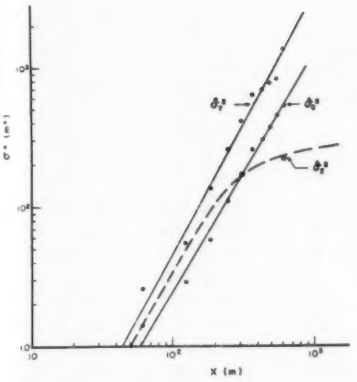


Fig. 4. Estimates of the variances, σ_c^2, σ_T^2, and σ_z^2 as a function of the distance from the source, X.

approximate model permits a rough estimate of σ^2_c. Let us assume that the effluent concentration within all plumes *of equal width* is on the average uniformly distributed across the plume and is discontinuous at the visual edge of the plume. Then the distribution of relative concentration is given by

$$X_{ci} \propto \frac{1}{w_i} \quad for \quad \eta \leq \frac{w_i}{2}$$

and (7)

$$X_c \equiv O \quad for \quad \eta > \frac{w_i}{2}$$

where w_i is the ith class interval of plume width w. Then the average relative concentration at η is given by

$$X_c(x, \eta, o) \propto \sum_{\eta \leq \frac{w_i}{2}} \frac{n_i}{w_i} \qquad (8)$$

where n_i is the frequency of w_i and the summation is over all plumes with half-widths greater than η. The distribution of X_c along η can be determined by repetitive use of equation *(8)* on the data while varying η and

$$\hat{\sigma}^2_c = \frac{\Sigma X_c \eta^2}{\Sigma X_c}, \qquad (9)$$

the summation extending over all values of η for which X_c has been calculated.

Evaluation of σ^2_z can be done directly from the values of relative concentration observed at various heights.

$$\hat{\sigma}^2_z = \frac{\Sigma X_z (Z - \bar{Z})^2}{\Sigma X_z} \qquad (10)$$

where $Z = \frac{\Sigma X_z Z}{\Sigma X_z}$ and X_z is the relative concentration observed at height Z.

Appropriate confidence limits may be attached to the estimates of variance derived from equations *(6)*, *(9)*, and *(10)* according to standard large-sample statistical techniques.

Analyses of the Data

The functional form of equations *(1)* and *(4)* is easily recognized as identical to the diffusion equations proposed by Roberts[8], Sutton[1], and Bosanquet and Pearson[4]. In each of these identity is established if it is assumed that the variances σ^2_c, σ^2_T, and σ^2_Z are a function of a power of the distance from the source. Then a test of the relationship

$$\sigma^2 = ax^p \qquad (11)$$

for each of these variances constitutes a test of these diffusion equations. Since equation *(11)* plots as a straight line on log paper a ready check of this equation is obtained by plotting ln σ^2 versus ln x. Such a plot for one experiment is shown in Fig. 4. The goodness of fit of the straight line to the plotted values of σ^2_c and σ^2_T may be judged from the fact that the linear correlation of ln σ^2 on ln x for these 2 curves is .994 and .993, respectively. Equation *(11)* appears to give an adequate representation of the dependence of σ^2_c and σ^2_T on x.

There is a very strong suggestion that σ^2_z does not follow equation *(11)*. Rather this variance appears to tend toward a constant, or a much reduced rate of increase, beyond x = 300 m. This observation is in agreement with visual measurements reported by Shorr[6] who concluded that $p_z \rightarrow$ o beyond x $\approx$ 300 m. is an acceptable first approximation to the true state of affairs. More experimental data are required to substantiate this point, but there appears to be little doubt that the diffusion becomes progressively more anisotropic with increasing distance from the source. If this is the case, modification of Sutton's equations by setting $C_z \neq C_y$ but retaining a constant *n* cannot adequately represent diffusion in stable atmospheres since n = 2 − p and p_z is neither equal to p_c or p_T nor is it a constant beyond x = 300 m.

Three measurements of the variance of the vertical distribution of concentration at 300 m. from the source are shown as a function of the Richardson Number in Fig. 5. Again more data are required but the implication that this variance is a nearly unique function of the Richardson Number is unmistakable.

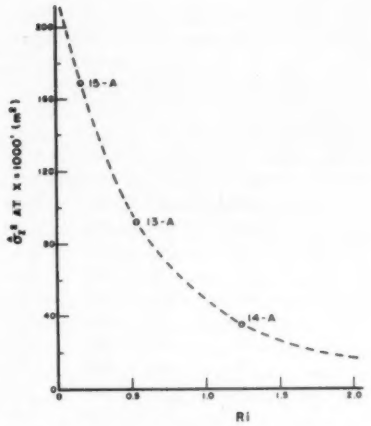


Fig. 5. Estimates of the variance of the vertical distribution of concentration, σ_z^2, as a function of the Richardson Number. σ_z^2 measured at 1000 ft. downwind from the source.

Turning now to the horizontal distribution of concentration, values of the a and p coefficients and the square of the linear correlations for ln σ^2_c, ln σ^2_N, and ln σ^2_T versus ln x are shown in Table I for 16 experiments. In each case equation *(11)* is substantiated, but a wide range of the diffusion coefficients obtains. On the basis of the wide variability of the p coefficients we may summarily reject the diffusion equations proposed by Roberts and Bosanquet and Pearson. Only Sutton's equation admits a variable exponent on x. But note that p_T varies from 1.39 to 1.93. This corresponds to a range of 0.61 to 0.07 for Sutton's *n*! Also, a_T which is equal to ½ of Sutton's diffusion coefficient, C^2_y, varies from .009 to .268 $m.^{2-p}$. These wide ranges of the diffusion coefficients hardly permit the assignment of 1 or 2 pairs of values which adequately portray all of the observed concentration distributions.

In order to assess the variability of the average concentration within these experiments, the axial concentration at x = 300 m. has been computed from equation *(4)* for each experiment. These values, appropriate to an emission rate of one gm./sec., are listed in Table II. The ratio of the extreme values of X_T/Q is about 25, *i.e.*, the average axial concentra-

TABLE I

Values of $r^2(\ln\sigma^2, \ln x)$, a, and p Derived for Each Experiment (Confidence Limits Assessed At 92% Level). Units of a = m^{2-p}.

Field Test No.	r^2_N	a_N	p_N	r^2_c	a_c	p_c	r^2_T	a_T	p_T
1-A	.989	.041 ± .003	1.45 ± .11	.987	.054 ± .011	1.33 ± .11	.991	.093 ± .013	1.39 ± .09
2-A	.986	.015 ± .004	1.70 ± .15	.989	.004 ± .001	1.96 ± .07	.999	.015 ± .002	1.83 ± .04
3-A	.990	.060 ± .005	1.77 ± .13	.890	.023 ± .024	1.37 ± .34	.991	.067 ± .016	1.75 ± .12
4-A	.997	.019 ± .008	1.64 ± .08	.989	.017 ± .004	1.63 ± .12	.995	.037 ± .006	1.63 ± .08
5-A	.985	.022 ± .003	1.48 ± .20	.940	.023 ± .012	1.47 ± .26	.985	.044 ± .012	1.48 ± .13
6-A	.969	.022 ± .014	1.66 ± .21	.973	.018 ± .001	1.58 ± .19	.976	.038 ± .014	1.66 ± .18
7-A	.987	.001 ± .000	1.99 ± .16	.980	.020 ± .006	1.43 ± .14	.984	.009 ± .003	1.72 ± .16
8-A	.995	.002 ± .000	1.93 ± .08	.989	.012 ± .003	1.62 ± .06	.996	.027 ± .005	1.89 ± .04
9-A	.991	.019 ± .004	2.00 ± .14	.992	.018 ± .004	1.54 ± .10	.999	.011 ± .002	1.78 ± .12
10-A	.987	.260 ± .056	1.39 ± .09	.980	.021 ± .001	1.78 ± .18	.999	.186 ± .028	1.55 ± .04
11-A	.958	.278 ± .040	1.51 ± .22	.996	.020 ± .000	1.72 ± .08	.975	.268 ± .010	1.55 ± .18
12-A	.986	.056 ± .016	1.76 ± .15	.987	.007 ± .002	1.92 ± .15	.994	.059 ± .014	1.80 ± .10
13-A	.989	.007 ± .001	1.85 ± .13	.986	.010 ± .003	1.69 ± .14	.992	.016 ± .004	1.79 ± .11
14-A	.999	.072 ± .007	1.93 ±.03	.998	.012 ± .002	1.55 ± .05	.999	.077 ± .014	1.93 ± .04
15-A	.963	.007 ± .001	1.80 ± .25	.988	.005 ± .002	1.92 ± .15	.987	.010 ± .003	1.88 ± .15
16-A	.984	.088 ± .025	1.55 ± .14	.986	.022 ± .009	1.73 ± .15	.993	.098 ± .019	1.62 ± .10

tion at x = 300 m. is about 25 times greater in Field Test 7-A than that observed in Field Test 14-A.

The diffusion coefficients listed in Table I are of course applicable only within the range of the observations from which they are derived, namely 200 to 2000 ft. However, a rational extension of these results to greater distances may be made under the following assumptions:

(1) The value of X/Q at x = 300 m. listed in Table II is correct.

(2) Within the range 300 < x < 3000 m. the diffusion is limited to the horizontal cross-wind direction only and proceeds as $x^{-p_T/2}$.

(3) Beyond x = 3000 m. the concentration of the effluent material decreases as $x^{-1/2}$ and the diffusion process is again wholly horizontal.

(4) The meteorological and terrain conditions are uniform within the times and distances under consideration.

The justification for these assumptions of the dependence of the variance, σ^2_T, upon x, or the dependance of concentration upon x, may be sought in Taylor's[7] theory of diffusion by continuous motions. According to this theory σ^2_T is given by

$$\sigma^2_T = 2v'^2 \int_0^T \int_0^t R(\xi)\, d\xi dt \qquad (12)$$

and when t is small, $R(\xi) \approx 1$, and

$$\sigma^2_T = v'^2\ T^2 \approx \frac{v'^2}{u^2} x^2. \qquad (13)$$

When t is large, $\int_0^t R(\xi)\, d\xi \rightarrow$ constant $= K$ and

$$\sigma^2_T = v'^2\ K\ T \approx \frac{v'^2}{u^2} u\, k\, x. \qquad (14)$$

Thus, the appropriate exponent on x in equation *(11)* tends to 2.0 near the source and to 1.0 at large distances. At intermediate distances the experimental values apply.

The dependence of uX/Q upon x for 4 experiments, derived from experimental values for $\frac{uX}{Q}$ at x = 300 m. and observed values of p_T according to the above assumptions are shown in Fig. 6. Since, by the complete elimination of vertical diffusion beyond x = 300 m., there is a tendency to overestimate concentrations beyond this distance, these values may be considered conservative. Also, the limits of 300 and 3000 m. for the discontinuous changes in p_T are somewhat arbitrary. However, this figure is probably substantially correct and illustrates very clearly the necessity for clear recognition of the strongly anisotropic nature of diffusion in stable atmospheres. If it were assumed that $\sigma^2_z = a_z\, x\, p_z$ and $p_z = p_T$ even though $a_z \neq a_T$, the resultant estimate of concentration would decrease as x^{-p_T} for all x and a very substantial underestimate of $\frac{uX}{Q}$ would result.

TABLE II

Values of X_T/Q At (x = 300 m., y = z = o) For Each Experiment. (Units of X/Q: sec/m^3).

Field Test No.	X_T/Q $\times 10^{-4}$	Field Test No.	X_T/Q $\times 10^{-4}$
9-A	3.49	1-A	1.60
10-A	1.08	2-A	1.33
11-A	0.84	3-A	0.71
12-A	1.14	4-A	2.01
13-A	1.38	5-A	1.25
14-A	0.76	6-A	0.63
15-A	16.8	7-A	0.88
16-A	1.79	8-A	11.1

So far we have considered only the long-term average distribution of concentration with regard to a coordinate system which is fixed with respect to the earth. In this system both variable transport (meander) and diffusive mixing contribute to the decrease of concentration with distance from the source. Since in stable atmospheres, the vertical distribution of concentration is independent of the horizontal cross-wind position of the plume we may evaluate the relative contribution of horizontal plume meander and diffusive mixing by considering the ratio of the axial concentrations X_c and X_T.

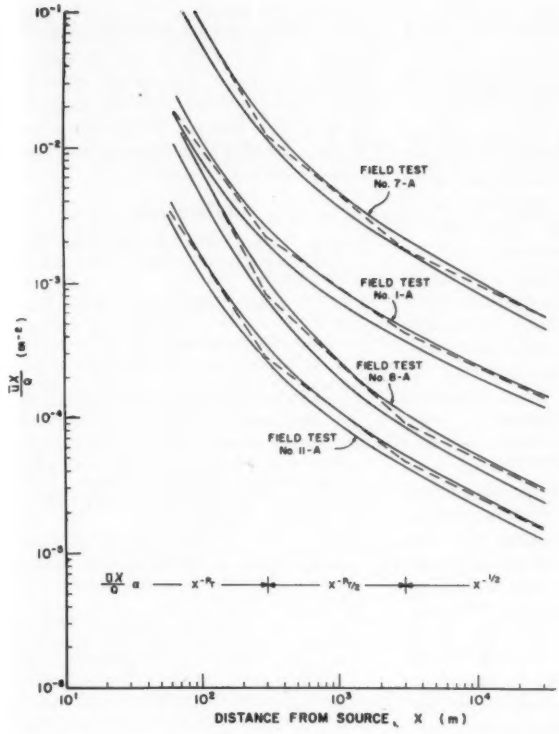


Fig. 6. Estimates of the decrease of axial concentration in continuous plumes emitted from an elevated point source as a function of the distance from the source. Range of observations: 60 to 600 m.

$$\frac{X_c}{X_T} = \left(\frac{\sigma_c^2}{\sigma_T^2}\right)^{3/4} = \left(\frac{\sigma_N^2}{\sigma_c^2} + 1\right)^{3/4} \qquad (15)$$

Values of $\frac{X_c}{X_T}$ for 16 experiments are listed for 3 distances from the source in Table III. The average axial concentration within the plume is as much as 8 times the average axial concentration in the fixed coordinate system but is generally only 1½ to 3 times greater.

Potential Hazards and Benefits

The emission of potentially harmful contaminants into stable atmospheres poses a somewhat paradoxical situation with regard to the height of release. If the material is released at or near ground level the presence of stable temperature stratifications is an undesirable situation since the low diffusive capacity of the atmosphere and generally low ventilation rates permit the existence of relatively high concentrations and dosages. However, if the material is emitted at substantial heights above ground level the problem of high concentrations near the source is obviated by the fact that the material does not come to ground level *so long as the stable temperature stratification persists.*

The absence of significant ground level concentrations near the source makes the stable case a very tempting one insofar as disposal of stack gases is concerned. This advantage is not to be had without cost, however, and the price that must be paid is the potential for relatively high concentrations at distant points. The establishment and dissipation of stable temperature stratifications follows essentially a diurnal cycle and with the dissipation of the temperature inversion the effluent material is generally mixed to ground level. This process, termed *fumigation* by Hewson[5], may occur at distances of the order of tens of miles from the source when the effluent has been carried to these distances in a stable atmosphere.

TABLE III

The Ratio X_C/X_T At 3 Distances From The Source.

Field Test No.	Distance from Source (m.)		
	200 m.	400 m.	600 m.
1-A	1.54	1.57	1.59
2-A	1.39	1.34	1.31
3-A	4.76	5.45	6.53
4-A	1.51	1.51	1.51
5-A	1.42	1.42	1.42
6-A	1.69	1.73	1.78
7-A	1.41	1.56	1.67
8-A	3.03	3.33	3.54
9-A	1.50	1.65	1.76
10-A	1.62	1.50	1.49
11-A	2.27	2.21	2.15
12-A	2.11	2.01	1.97
13-A	1.62	1.68	1.72
14-A	6.77	7.71	8.29
15-A	2.17	2.09	1.88
16-A	1.59	1.54	1.51

The processes of fumigation are not yet well specified, primarily because the changeover from stable to unstable temperature stratifications is frequently accompanied by marked changes in the motions of the lower atmosphere. However, as a useful model we may assume, with Hewson, that the effluent material is uniformly mixed from its initial height to ground level at the site of the fumigation. Then the concentration at ground level is approximately $\frac{Z_o}{H}$ times the concentration prior to mixing, where H is the height of the centerline of the plume segment and Z_o is a representative measure of the vertical thickness of the plume prior to the onset of fumigation. Since the time required for mixing of the effluent to ground level is not long enough to include an appreciable fraction of the period of the long-term meander of the plume, the initial concentration in the plume is best approximated by X_c. Then a representative measure of the ground level concentration during the fumigation process is given by

$$X_G = X_c \frac{Z_o}{H}. \qquad (16)$$

The ratio $\frac{Z_o}{H}$ is, at most, one (the plume is brought directly to ground level) and for normal stack heights this ratio is probably seldom less than about ⅕. Assuming the upper limit, the ground level concentration at x = 10 km. during fumigation in connection with Field Test 7-A can be approximated by

$$X_G = X_c = 1.7 \approx \frac{Q}{u} \times 10^{-3} \qquad (17)$$

Whether or not this concentration is hazardous depends upon the permissible limits for the effluent material at the site of the fumigation.

Estimates of ground level concentration derived by these methods are of course applicable only to longer-term averages, (the case of chronic exposure). For very short-term aver-

age concentrations (acute exposure) the effluent concentration in individual puffs must be considered and these may exceed the longer-term average concentrations by an order of magnitude or more.

Conclusions

The foregoing observations of the diffusion and transport of stack effluents in stable atmospheres provide several significant pieces of information:

(1) The concentration of stack effluents, when measured over a grid fixed with respect to the ground, is decreased significantly by large-scale meander. The large-scale motions which induce plume meander must be taken into account when specifying this distribution.

(2) The diffusive capacity of stable atmospheres is quite variable from one time to another and no single set of diffusion parameters can be assigned to stable atmospheres *per se*.

(3) Sutton's diffusion model appears to be adequate for the specification of the horizontal diffusion rate but fails in the specification of the vertical diffusion rate. This failure causes Sutton's model to underestimate the concentration at moderate and large distances.

(4) The vertical distribution of concentration appears to depend strongly upon the Richardson Number.

The selective emission of stack wastes into stable atmospheres must be approached cautiously since the advantages of low ground-level concentrations near the source may be offset by relatively high concentrations at more distant points.

Acknowledgments

The extensive experiments and analyses upon which this paper is based were made possible by the wholehearted cooperation and enthusiastic efforts of the following members of the Atmospheric Physics Operation: R. L. Conley, Jr., J. J. Fuquay, D. M. Hughey, P. W. Nickola, M. F. Scoggins, C. L. Simpson, and B. Shorr. The author is deeply indebted to these gentlemen, not only for their assistance, but also for their many suggestions and criticisms which were invaluable in these studies. The guidance of Professor H. R. Byers in this work is also gratefully acknowledged. The work reported here was performed under Contract #W-31-109-Eng-52 between the Atomic Energy Commission and General Electric Company.

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Design and Interim Meteorological Evaluation of a Community Network for Meteorological and Air Quality Measurements*

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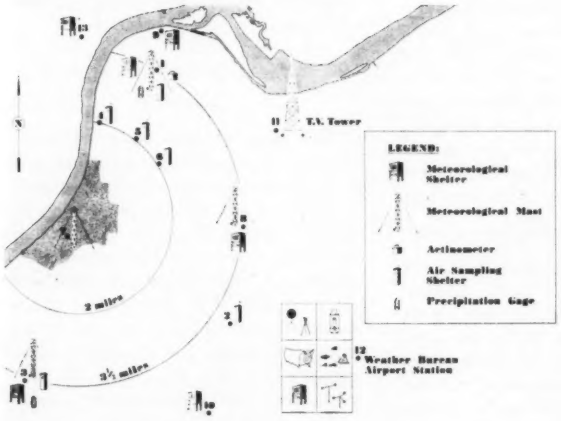
An air quality and meteorological measuring network was designed and installed at Louisville, Kentucky in connection with a joint study of air pollution undertaken by city, Jefferson County, state, and federal agencies. The study was centered in a neighborhood consisting essentially of presumed source and principal receptor areas. The main source area of interest was considered to be a concentration of large industrial plants located in an industrially zoned area on the southwest side of Louisville. This area, because of its development as a wartime synthetic rubber manufacturing center, is known as Rubbertown. The principal receptor area was considered to be the so-called West End residential area, north and northeast of Rubbertown. Objectives of the study included the determination of *(1)* air quality in the principal receptor area and in secondary areas of interest within the community, *(2)* source areas of pollution found in the principal receptor areas, and *(3)* the fraction of the pollution found in the principal receptor area contributed by the presumed main source area. The network design, based on the objectives of this particular study as well as several meteorological considerations, appears to be adequate enough to provide significant descriptive data concerning air flow and air quality patterns.

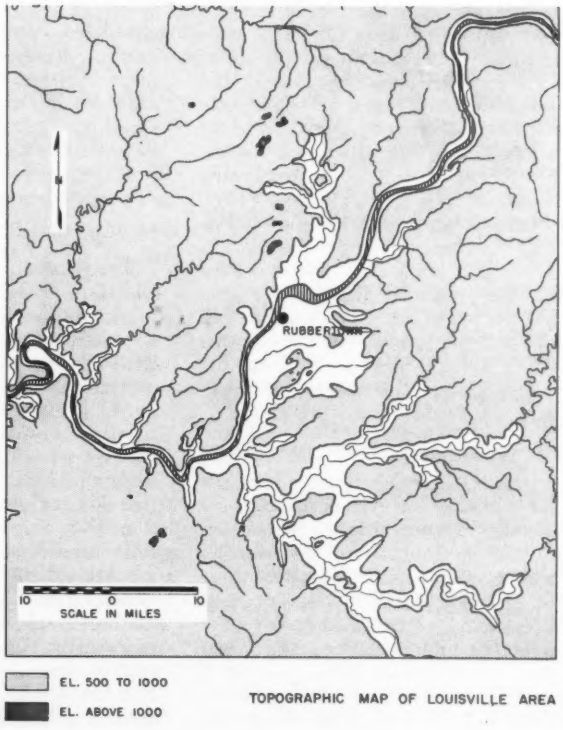
* Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

Network Design—General

The design of the air quality and meteorological network resulted from four basic considerations. The first was the relative locations of the presumed main pollution source and receptor areas (Fig. 1) which were to be given special attention in the study. Accordingly, the main axis of alignment of the network coincided with the axis linking these source and receptor areas (Fig. 1). Air quality and meteorological network stations were concentrated in and around these 2 areas.



(Above) Fig. 1. Meteorological and Air Quality Measurement Network at Louisville, Kentucky. No. 7 is located in Rubbertown. No. 1, 4, 5, 6 and 9 are in the West End.



(Right) Fig. 2. Principal Topographical Features in Vicinity of Louisville, Kentucky.

The second consideration in the network layout was the expected frequency of winds from various directions. The wind direction is an obvious primary determinant of the direction of the transport of pollutants. From a study of existing Weather Bureau records of the Louisville area, the frequency of winds favorable for air transport from the main source towards the principal receptor area was expected to be reasonably high. In fact, the appropriate wind direction was frequent enough so that neither special precautions nor an unusually tolerant attitude toward low efficiency in air quality measurement would have to be adopted.

Topography was the third consideration. Topographical features (Fig. 2) were noted in order to determine whether local anomalies might be expected because of surface features. Some channeling of the air flow was expected because of the ridge west of the river and the point of high ground projecting towards the main study area from the south (Fig. 2). Other less obvious features probably would influence the flow. These influences were expected to enhance the frequency of winds in the direction of the network alignment.

The fourth consideration involved source-receptor spacing. Air transport and diffusion processes occurring between pollutant source and receptor vary depending upon time and space factors. However, no complications were foreseen from this cause. The logical reasoning used in defining the source and receptor areas probably eliminated difficulties that would have occurred in a more complicated situation.

Consideration of these four points led to a network design consisting primarily of a main alignment axis linking the presumed main source area and the principal receptor area. The air sampling points were located primarily along this axis, with the points of meteorological measurement bracketing this region in a loose array.

Network Design—Sector Information

One of the design features included the provision for greater detail of information concerning air flow from the main source toward the principal receptor area. For this purpose three air sampling stations (No. 4, 5, and 6 — Fig. 1) were located on the inner arc. The middle station, No. 5, was sited on the main axis, and the 2 flanking stations were sited at points about 20° of azimuth to either side of the axis as viewed from the source area. The spacing of these stations was intended to provide the widest sector coverage feasible without the pollutant plumes avoiding detection by passing between stations. The 3 stations were approximately equally spaced to improve later estimate of the cross-wind gradients of concentration.

Network Design—Range Information

Within the same sector of main interest, an air sampling station was located on the outer arc along the principal axis of the network (No. 1 — Fig. 1). This station was established to provide measurements of air quality at a point approximately double the distance of the inner arc from the main source area. In the original design, the location of flanking stations on the outer instead of the inner arc was considered equally useful. The adopted locations (No. 4 and 6) on the inner arc prevailed for practical reasons. Comparative measurements between stations on the 2 arcs within the primary sector would provide information on the variation of surface concentrations with distance, when the transport was downwind from the main source area and parallel to the main axis of the network. The distance to the nearest sampling stations on the inner arc (about 2 miles) was greater than the calculated average distance of maximum concentration (even from the taller individual sources in the principal source area) during lapse or unstable conditions. Therefore, it would be possible to compare measured and predicted decrease of concentration of particular pollutants with distance.

Network Design—Control Information

The determination of air pollutant emissions which are locally controllable within a community depends on the determination of pollutant contained in the mass of air prior to its arrival over the community. In order to determine the air quality in the primary network sector unaffected by emissions from the main source area during periods of wind flow along the principal axis of the network, a station (No. 3 — Fig. 1) was located near the axis at a point on the outer arc beyond the main source area as viewed from the receptor area. Air quality at this station could be compared with that in the principal receptor area to estimate the contribution of pollution from the main source area.

Network Design—Comparison And Prediction Factors

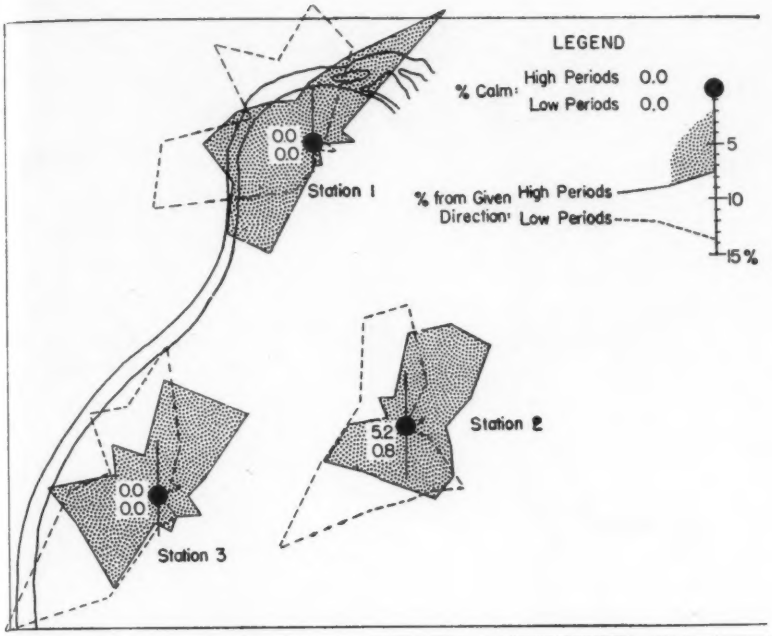
All of the air sampling stations were sited at one of two distances from the main source area. This made it possible to compare measurements from any of the stations on a common arc without the added complication of large variations in distance from the presumed source. Measurements at stations on the inner arc (No. 4, 5, and 6) during suitable periods could be compared, and measurements of air quality at stations on the outer arc (No. 1, 2, and 3) could likewise be compared. This would afford an internal check on the validity of the results obtained. Thus, conclusions drawn from study and analysis of the data from the concentrated grouping of stations 1, 4, 5, 6, and — to some extent — 2 with respect to the main source area could be used in making predictions, which would be susceptible to internal check at stations 2 and 3 under appropriate meteorological conditions. Station 2 was intended to be located approximately equidistant from both the given main source area and an industrial concentration in another part of the city. This made it possible to make a comparison of still a different kind, although for practical reasons the actual location of station 2 was some 20° of arc south of the optimum position.

Network Design—Operating Schedule

The network was designed to operate on a continuous schedule, with at least one common pollutant measurement at all air sampling stations. Three reasons for this requirement may be given: *(1)* The normal variability of meteorological conditions often means that the largest practicable number of data are desirable to define the mean for any given set of conditions; *(2)* any kind of interrupted data collection scheme is likely to introduce a bias in the data collected that is difficult to define; and *(3)* continuous or serial measurements can provide the elements of a controlled experiment through selection of data for analysis.

Network Design—Air Sampling Stations

The air sampling stations were sites for the measurement of a variety of air pollutants. The instrumentation has been largely described elsewhere.



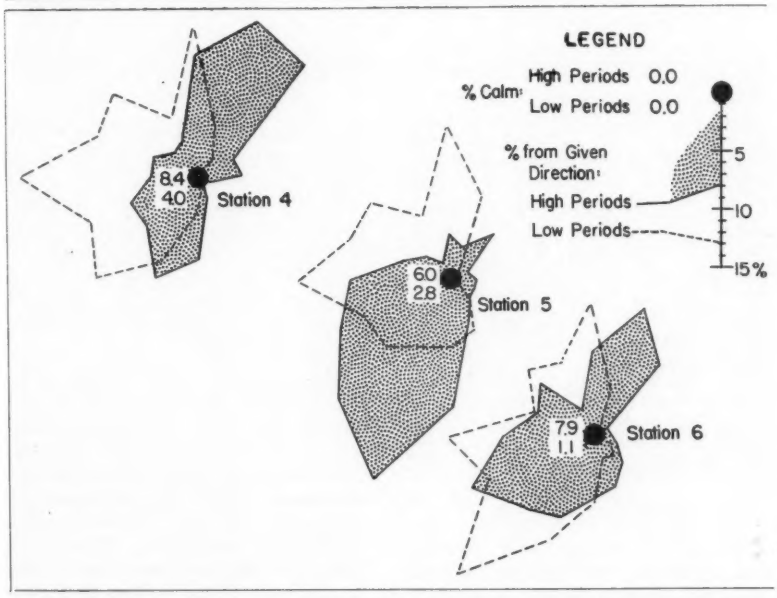


Fig. 3a. Winds During Periods of High and Low Particulate Concentrations at Stations 1, 2 and 3 in June 1956.

Fig. 3b. Winds During Periods of High and Low Particulate Concentrations at Stations 4, 5 and 6 in June 1956.

For the present purpose, this instrumentation may be summarized as follows: The common measurement at all air sampling stations referred to above was the weight of particulate material/unit volume of air flow as collected by high-volume samplers. These samplers drew about 25,000 ft.^{3} of air/run through a 63 in.^{2} filter area. The samplers operated continuously for three 8-hr. periods daily, beginning at about midnight, 8 a.m., and 4 p.m. The material collected by the samplers was further analyzed for benzene soluble fractions, as well as in other ways. In addition, continuous measurements of soiling index and SO_2 concentration were obtained at several locations. Other air quality measurements included dust-fall and selected gases. Only *concentration* of particulate matter — that is, weight of particulate matter caught on the filter/unit volume of air flow — will be discussed here.

Network Design—Meteorological Stations

The primary purpose of meteorological measurements in this study was to determine patterns of air flow, and only incidentally to describe the behavior of any one meteorological element at any one point. It was, therefore, unnecessary to have a one-to-one correspondence between air quality sampling stations and points of meteorological measurements. The surface wind measuring stations were located in more or less an *A* pattern, straddling the point of high ground projecting towards the study area from the south. Stations 3 and 12 form the bases of the *A* and station 1, the apex; stations 7 and 8 completed the pattern. Station 7 was a pre-existing installation of E. I. DuPont de Nemours and Company, from which data were made available for this study. Station 11, the WHAS-TV tower, was equipped with wind instruments mounted at the 524 ft. level. Thus, a measure of wind relatively uninfluenced by details of the underlying surface is also obtained.

Stations 9, 10, and 13 were solely hygrothermograph stations. Station 9 was located near the river, while No. 10 and 13 were located at comparatively high surface elevations. Stations 1, 3, and 8 were also equipped with recording hygrothermographs. Hourly readings for all standard observed weather elements were available from station 12, the Weather Bureau Airport Station. Station 1 was equipped with a recording radiometer. Stations 1 and 8 were equipped with recording rain gages. This layout, taken together with upper air soundings at Peoria, Dayton, Nashville, and other nearby weather stations, was intended to provide data on the interrelated air flow and temperature patterns over the study area on a meso-meteorological scale.

Evaluation of Design Features

Of the features incorporated into the network design, those of sector information and operating schedule will be given some elaboration here by way of example.

Sector Information

Sampling stations 4, 5, and 6 (Fig. 1) were arrayed normal to the main

network orientation to detect the stream of air passing from the principal source area to the receptor area of interest.

The question may be asked: Are there occasions when the stream of presumably pollutant-laden air from the principal source area passes between or around these stations and reaches areas beyond, with no indication of this air stream at any of the closer stations? A comparison of measurements at station 1 with those obtained at 4, 5, and 6 can provide a qualified answer to this question. The data for the months of June, July, August, and October of 1956 were examined to find cases where *(a)* total particulate concentration at station 1 was higher than at 4, 5, or 6; and *(b)* the air flow was from the principal source area toward station 1. Fourteen cases, or approximately 4% of the sampling periods, were found to satisfy both requirements. Twelve of these occurred during the morning or evening periods, with indications of a stable lower atmosphere. For these cases, a reasonable assumption of diffusion parameters leads to the prediction that the maximum ground concentration from the elevated sources in the source area should occur near and beyond the more distant sampling station. On this basis, it is considered likely that the stream of air carrying the pollutant passed over the near stations rather than between them. Of the 2 daytime cases, the concentrations of particulate material at the more distant station were hardly the same (4% higher) as at one of the nearer stations; the difference is within the estimated sampling error. An estimated 25 daytime cases of flow along the axis occurred during the months considered. Only these 2 equivocal cases, or 8% of the total, would tend to disprove the hypothesis that the inner arc of stations detects the pollutant-laden air stream. It is concluded that the inner arc of stations did function as a detective screen in at least 90% of the cases in which it would be expected to do so, disregarding possible complications from unknown sources.

A qualitative inference regarding the presence of sources outside the main source area may be drawn from a comparison of monthly median concentrations of particulate matter at stations 1 and 5. The calculated decrease of concentration with distance from a specific source under lapse conditions tends to approach the reciprocal of the distance squared, over the range of distances here considered. For all 3 sampling periods of the day, the 3 median concentrations at station 1 average only slightly lower than those for station 5, ranging from 76 to 106% of the station 5 median values. This is true even for those months and periods during which the air stream from the Rubbertown source area was most frequently along the main network axis towards stations 5 and 1.* It seems then that one must reckon with sources outside the main source area.

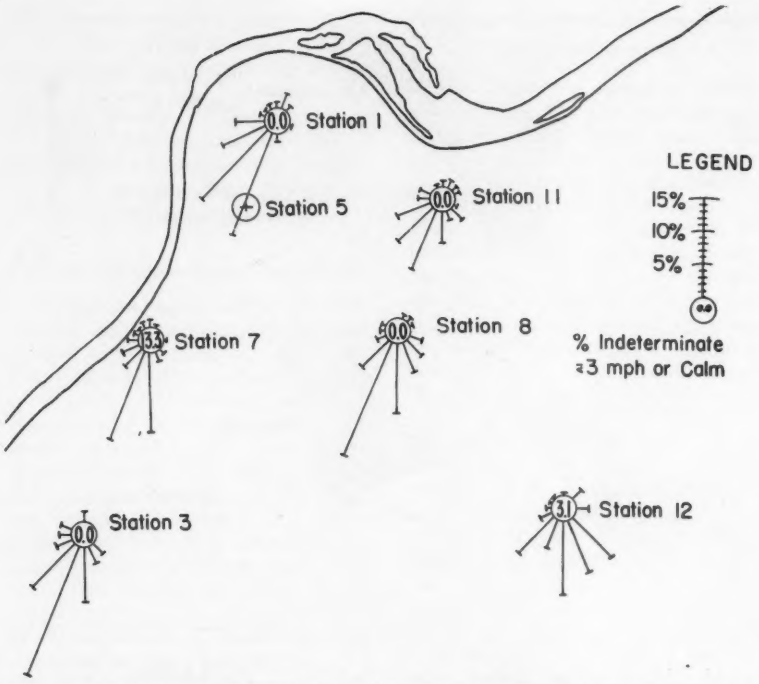


Fig. 4. Winds During Night-time Periods of High Particulate Concentrations at Station 5 in July 1956.

Operating Schedule

The utility of this design feature can be demonstrated by two related examples of analysis.

Given a continuous series of measurements, the sampling periods of interest may be defined as those in which the more extreme values of air quality were measured. Accordingly, for each month, and each of the 3 sampling periods/day, the 8 (out of 30) periods of highest and lowest particulate concentration measured at each sampling station were selected. The common measure at all stations provides the means for a direct comparison of air quality between stations of the network. The observed winds were taken from the nearby surface wind station network and tabulated to provide an approximation of the surface air flow at the sampling stations during these 24 periods of high and low concentration during the month.

The patterns for June 1956 (Fig. 3a and 3b) were obtained by the method described. At all stations, the periods of high pollutant concentration were associated with winds predominantly from the northeast or southwest quadrant. Wind direction frequencies for periods of low concentration show a considerable overlapping with direction frequencies for periods of high concentration, although generally northwest winds were more frequently associated with low concentrations, and easterly winds (northeast at station 2) occurred primarily with high concentrations. These tendencies reflect 2 factors: *(1)* Locally, the position of urbanized areas with respect to the sampling stations; and *(2)* on a larger scale, the well-known tendency through the east-central United States for unstable northwest winds to occur following cold frontal passages, whereas easterly winds occur most

* This condition was considered to exist whenever the station 5 median concentration exceeded the concentrations at the flanking stations 4 and 6.

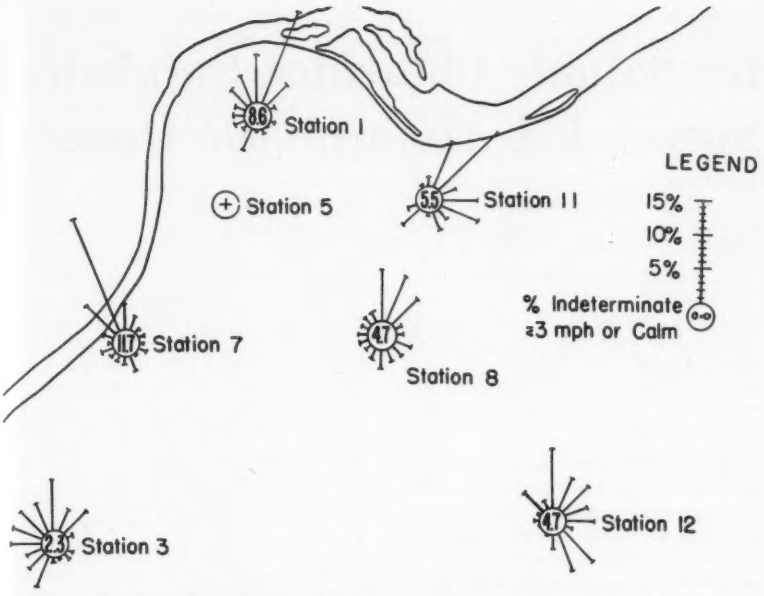


Fig. 5. Winds During Night-time Periods of High Particulate Concentrations at Station 5 in October 1956.

often during or following the passage of centers of high pressure, with associated light winds and stability of the air mass.

At stations 4, 5, and 6, (Fig. 3b) the particular direction of maximum frequency in the southwest quadrant shifts from slightly west of south at station 4 to west-southwest at station 6. This change of direction could indicate a source region for the substance being measured, although more information is obviously needed to resolve the point. The attenuation of the lobe of northeasterly winds at 5 during these periods of high concentration is not clearly understood, although the distribution of nearby sources and the predominance of the southwestern quadrant are plausible causes.

Data for July 1956, a month of prevailing southwesterly flow, has been used to show a different type of information (Fig. 4). Defining periods of interest as before to be those in which the more extreme values of air quality were measured, the air flow during periods of interest can be described. Sixteen sampling intervals of highest total particulate concentration measured at station 5-8 from each of the 2 sampling periods 1600-2400 and 0000-0800 — were selected, and the hourly winds observed at all the wind stations were tabulated.

The wind direction frequencies at station 11, the TV tower, most nearly represent the general flow of air over the area. Station 3 shows almost half the winds from the single direction, south-southwest; and station 1 shows a similar grouping, centered between south-southwest and southwest.

At station 12, however, a third of the winds were from the southeast or south-southeast. The winds at stations 1, 7, and 3 exhibit channelling by the river valley, while the southeast winds at the airport station are believed to be the result of the combined influences of topography and thermal differences between the urban and nonurban areas.

The 16 sampling periods of high concentration at the same station and for the same times of day were also selected for the month of October (Fig. 5). This month was chosen because the dominant flow was from a northeasterly direction, as shown by the 525 ft. (TV-tower) wind observations. The airport station *(12)* again showed an anomalous lobe of southeast winds, while station 1 showed a maximum frequency from the north-northeast and north. Station 3 showed no single preferred direction, although the northwest quadrant was dominant. These differences in wind direction from one station to another during the night-time periods when pollutant concentrations are high at station 5 illustrate that no single direction of air motion applies over the whole area of the network.

These examples of analysis serve to show *(1)* certain significant associations between wind direction and air quality, and *(2)* air flow patterns that exist during periods of particular interest. It would have been difficult to attain similar results if any sort of pre-selection of sampling periods, by meteorological or other means, had been employed.

Summary

An air quality and meteorological measuring network was designed to serve particular needs in the study of air pollution in the city of Louisville, Kentucky. Preliminary results indicate that the network data do qualitatively describe the air flow and air quality patterns. This qualitative understanding was necessarily preliminary to more quantitative descriptions.

Acknowledgments

The authors acknowledge the contribution of Mr. A. C. Stern, Chief, Community Air Pollution Program, in maintaining an atmosphere in which a novel approach to an air pollution problem is being worked through. The liberality of Dr. A. T. Rossano, Jr., Technical Director of the joint Special Air Pollution Study of Louisville and Jefferson County, both with respect to arranging graceful compromises in a complex cooperative effort and with respect to the use of air quality measurements, is also appreciated.

Estimation of Water Soluble Chlorides, Sulphates, and Nitrates in Suspended Atmospheric Dusts*

CHARLES GELMAN

Special Air Pollution Study of Louisville & Jefferson County

Louisville, Kentucky

As part of a program of atmospheric dust identification it was desired to determine the amount of water soluble chlorides, sulphates, and nitrates in these dusts. The dusts examined were air suspended material collected on filter paper by use of a high volume air sampler. Early in the study it was found that some methods widely in use for this type of determination sometimes gave erroneous results when applied to Louisville samples.

The present report will deal with modification of sampling technique, changes in methods for chloride and sulphate determination and with a method for the estimation of nitrates.

Sampling

Suspended dusts are collected from air using an air mover similar to that on a vacuum cleaner. The dust samples are collected on a flat sheet of filter paper. Initially glass fiber filter paper was used as the collecting medium. These papers are made using a resin binder and then flash fired to remove the binder. The batch of papers we first received was relatively free from soluble chlorides, sulphates and nitrates. Later batches of paper were found to be extremely high in water soluble chloride. The quantities of these materials initially present in paper were larger than the amount of material which would be found in a typical air sample. The variation in amounts of chloride between different sheets within the same batch was also high. The manufacturer explained the change as resulting from the use of a different grade of glass fiber. Subsequent glass fiber papers sent us were represented as being low in chloride content, however, the values were high enough to make these papers unacceptable for our use. Table I gives a summary of materials found in different batches of glass paper. These batch designations are our own and don't correspond to production batches.

The sampling medium was changed to Whatman #41H filter paper. This paper generally exhibits good physical characteristics for dust sampling although it may develop high resistance to air passage under high loading conditions[1, 2]. Type 41H paper was found to be low in benzene solubles, water soluble chlorides, sulphates, and nitrates (Table I). The major difficulty encountered in the use of the paper was in weighing it. Since cellulose is hydroscopic, significant variations in weight of a sheet of paper with relative humidity are noted. This variation was minimized by keeping the relative humidity of the balance room at constant humidity. This was inexpensively accomplished by use of a dehumidifier, humidistat, water spray, and relay. Since 41H paper is considerably less expensive than glass paper the savings in cost of paper have paid several times in a year for the humidity control equipment. The balance room was air conditioned during the summer because of the heat developed by the dehumidifier.

Extraction

It is necessary to first remove organic materials from samples before determining water soluble inorganics. With both 41H and glass paper low values of water soluble anions were found if some of the organic material was not first removed by benzene extraction. Apparently tarry materials collected in air samples inhibited the solution of inorganic salts in water. Removing the organic materials by firing the samples at 500-600°C. was not a satisfactory procedure. On both types of paper loss of sample occurred. On glass paper, chlorides were lower after firing the organics in a sample than the blank sheet before firing. The inorganic salts may fuse to the glass fibers in the paper even at this comparatively low temperature, to become water insoluble. In cases where it is necessary to use glass paper it would appear preferable not to fire paper to remove organics because of possible losses in inorganics. A similar loss was noted when firing samples collected on 41H paper. In this case the materials of interest may combine with silica present in samples and other chemicals to form insoluble glasses.

The reader is referred to articles by Keenan[3] and Silverman[4] for alternate procedures of sample treatment.

Preliminary Treatment

Spectrographic analysis of dust samples have sometimes shown the presence of large amounts of iron, calcium, copper, and lead as well as other metals in lesser quantities[5]. Some of these cations interfere with procedures later described. An ion exchange resin is used for their removal.

The procedure adopted for the extraction of water soluble inorganics is as follows: (1) ½ sheet of sample paper is extracted with benzene in a soxhlet extractor for 6 hr. (2) the sample is dried by evaporation (3) 50 ml. distilled water are added to the sample in a wide mouth erelmeyer flask (4) this is brought to a boil and simmered for 5 min. with gentle agitation (5) the extract is filtered through previously washed 41H paper and the extraction is repeated with a second 50 ml. portion of water (6) the volume is adjusted to 100 ml., approximately 1 g. of Amberlite IR-120(H) is added and the solution allowed to reach equilibrium overnight (7) portions of the extract are decanted for use in analysis as later outlined.

Chloride Determination

The use of a silver turbidimetric procedure[6] for estimation of chlo-

* Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

ride resulted in values high as compared with a mercurimetric titration[7]. Since the presence of sulphide in our samples was indicated, it was felt the high results could be explained by the formation of silver sulphide. The mercurimetric procedure[7] was adopted since there appeared to be less interferences and the procedure is more convenient and rapid. In this procedure 50 ml. of the water extract was treated with 3 drops of 30% hydrogen peroxide and the solution then titrated with mercuric nitrate using a diphenylcarbazone indicator. The peroxide treatment is necessary to oxidize any sulphites present in the sample. Ferric ions will interfere in this procedure but are removed by the preliminary treatment of the extract with ion exchange resin.

Sulphate

The water soluble sulphates are determined using a modified turbidimetric procedure[6]. Some difficulty was encountered because of a yellow coloration of water extracts which led to high values in the turbidimetric determination. The resin treatment of the extract effectively removed this color. The color may have been the result of ferrous chlorides present as such or formed from ferrous sulphide. The initial water extracts did show large amount of ferrous ion present. On standing, a solution of ferrous sulphide and sodium chloride develops the same color as was found in our samples presumably due to the dissociation of FeS to form $FeCl_2$. The color in extracts of air samples became similarly more intense on standing.

In the sulphate determination 10 ml. of sample extract are added to 10 ml. of water in a 100 ml. erlenmeyer flask. To this is added 1 ml. of 10 N HCl and 1 ml. of a 1 to 2 glycerin alcohol mixture. The solutions are mixed and the flask placed on a rotary agitator. Approximately 0.25 g. of barium chloride is then measured into the flask with an appropriately sized scoop and the flask shaken for 1 min. About 12 samples may be conveniently handled at one time. After 40 min. the optical density is determined at 500 μ. A Spectronic 20 colorimeter and 1 in. cuvettes were used. A calibration curve from known amounts of sulphate is determined in a similar manner in the range of 100-1000 mmg. in 10 ml. of solution. If total sulphur as sulphates is desired the sample may be first treated with some bromine water, the solution heated to expel excess bromine and the sulphate determination made as above. The uniform shaking with a mechanical agitator was found necessary to obtain reproducible results.

Nitrates

Several methods were examined for the determination of nitrates. The phenyldisulphonic acid method[8] and the 1,4 xylenol method[9] depend on the formation of nitrated derivatives in the presence of nitrates. In the presence of nitrites not only the normal nitrated derivatives are formed but also complex quinoid structured compounds[10]. In the 1,4 xylenol procedure the nitrated derivative is concentrated in toluene by extraction and then extracted in a caustic solution as the sodium salt. Using nitrite in place of nitrate in this procedure one finds that the caustic will extract only part of the compounds from the toluene layer. The reaction in this procedure normally proceeds as follows:

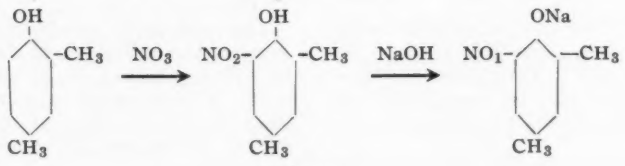


Fig. 1.

In the case of nitrite in addition to the above type of reaction other reactions also take place. Probably the nitrite reacts to give the following quinoid type compound as at least one product:

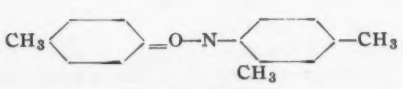


Fig. 2.

In the presence of nitrite, results in the above determination are high (Table II). Assuming a molar reaction in the same manner as nitrate the results are 16% lower than theoretical as would be expected because of the competing reactions. Table II also lists other interferences in this method. The presence of sulphide and sulphite lead to low results. Colored organic compounds such as picric acid which are not removed by the extraction procedure will lead to high results.

The difficulties in obtaining accurate results in the presence of nitrites were viewed as important. Although it was found that in most instances the amount of nitrite present in a given sample was only 1-2% of the amount of nitrate present, some samples did show nitrite as the predominant of the two. Since in this work we were interested in the unusual rather than the average this shortcoming of the 1,4 xylenol method was of major concern.

Reduction & Diazotization

The determination of nitrate by first reducing it to nitrite and determining the amount of nitrite has been proposed by several investigators. Bray[11] suggested the use of zinc and manganous chloride at a pH of 2.0 to effect this reduction. Woodward[12] recommended the use of zinc at a pH of 4.0-5.0. Nelson[13] reported a procedure for determination of nitrates in soil using the method suggested by Bray for reduction. This method used sulphanilic acid and alpha naphthylamine for detection of nitrite. The method is subject to many interferences[14] and was found difficult to reproduce.

The method developed for the determination of nitrate is based on the reduction of nitrate to nitrite, formation of a diazonium derivative of benzenesulphonilamide and then coupling to form a diazo dye. The optimum conditions for the latter reactions are discussed by Shim[15].

Procedure for Nitrate Estimation

Reagents

Dry Reduction Powder: Mix together 3.5 g. of purified diatomaceous earth, 0.66 g. manganous sulphate, and 0.4 g. finely powdered zinc.

Buffer: Dilute 21 g. citric acid and 1 ml. conc. HCl to 1 *l.* with distilled water.

Sulphanilamide: To about 500 ml. distilled water add 30 ml.

conc. HCl, add 3 g. of p-benzenesulphanilamide and dilute to 1 *l.* with water. This reagent is prepared daily.

Dye solution: Dissolve 25 mg. N(1-Naphthyl)-ethylenediaminedihydrochloride in 25 ml. water. The concentration of this reagent is not critical and solution is made with an appropriately sized scoop. The solution is prepared immediately prior to use.

Resin: Amberlite IR 120(H).

Determination

To 10 ml. of buffer solution add 1 ml. aliquote of extracted sample previously treated with resin. Add 1 scoopful (50 mg.) of reduction powder. Swirl on mechanical agitator for 1 min. Filter through good grade of filter paper into a cuvette containing 10 ml. sulphanilamide reagent. Wash with 5 ml. water. Add 1 ml. dye solution to cuvettes and mix thoroughly. Allow color to develop at least 2 min. and then determine optical density at 545 μ. Run blank sample and subtract value from unknowns.

A standard curve is prepared using known amount of nitrates. Using a Spectronic 20 with 1 in. cuvettes a satisfactory curve is obtained in the concentration range of 2-75 mmg. as nitrate in 1 ml. of sample. It was found convenient to determine 12 samples at one time. The dye solution was prepared before each series of determinations. It is possible for a laboratory technician to determine about 100 samples in a day.

Large amounts of iron and calcium and trace amounts of lead interfere with this procedure. The preliminary treatment of samples with the ion exchange resin effectively removed these interferences. Since the method basically determines nitrite, this must be initially determined or removed from the sample. To destroy nitrite add a crystal of ammonium chloride to the sample and gently heat to expel excess reagent. Nitrite may be determined and then an appropriate correction applied to nitrate value.

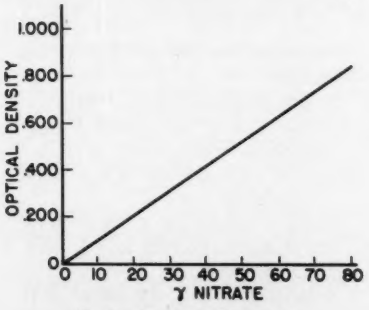


Fig. 3. Nitrate calibration.

Essentially the same procedure as outlined above is followed for the determination of nitrite omitting the dry powder and the initial buffer. The nitrite determination is 10 times more sensitive if a 10 ml. aliquote of sample extract is added to 10 ml. of the sulphanilamide reagent solution. After 5 min. add 1 ml. dye solution and proceed as above. A separate calibration curve is prepared using standard solution of nitrite.

TABLE I
Materials in Blank Filter Papers (Micrograms per 7 in. x 9 in. sheet)

	Glass #1	Glass #2	Glass "special"	Whatman #41 H
Benzene Extract	2.4	1.6	1.5	0.9
Chloride	1030 ± 75	29000 ± 3700	16500 ± 1800	195 ± 23
Sulphate	ca. 100-150	1550 ± 250	1630 ± 300	115 ± 85
Nitrate	trace	trace	trace	trace

TABLE II
Interferences — 1, 4 Xylenol Method

Gamma nitrate added	Interference	Gamma nitrate found	% Error
40.4	20 γ Na_2SO_3	37.0	−8.8
40.4	28 γ Na_2S	33.0	−18.5
40.4	16 γ NO_2—	54.0	+33.4
40.4	20 γ picric acid	43.0	+6.2

TABLE III
Reproducibility of Nitrate Method

Nitrate added	Nitrate found	Average	Dev.
12.5	12.5		
12.5	12.5		
12.5	12.5	12.5	0.6
12.5	14.0		
12.5	11.00		
24.5	25.0		
24.5	26.0		
24.5	24.5	24.5	0.9
24.5	23.5		
37.0	37.0		
37.0	35.5		
37.0	38.5	37.0	1.6
37.0	39.0		
37.0	40.0		
50.0	50.0		
50.0	48.5		
50.0	54.0	51.0	2.8
50.0	47.0		
50.0	55.0		

The method for nitrate estimation is accurate within 2-5% in the range of 2-75 mg./*l.* in 1 ml. of water extract. This accuracy is satisfactory since the determination of collection volume is subject to considerably greater error.

The methods outlined here have been in use on a routine basis in Louisville for about 6 months. The procedures are simple enough to be followed by non professional personnel.

Acknowledgement

The author wishes to express appreciation for the contributions and

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The Role of Motor Vehicle Exhaust in Smog Formation*

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Smog, in the sense it is now commonly used, is not just a mixture of smoke and fog, but any abnormal concentration of matter in the atmosphere which is sufficient to harm or annoy people. This broad definition is unfortunate because we then have to define the kind of smog we are talking about. To one person it may be the odor of a slaughterhouse; to another, the eye irritation typical of that experienced in Los Angeles. It may be the smoke and fumes that crowd into the air vent of one's automobile as he follows a bus down the avenue; again, it may be a high concentration of toxic gases in a semi-enclosed space.

No matter how you define it or which smog manifestation bothers you, you can find a relationship between smog and some constituent of auto exhaust—the aldehydes in exhaust stink; carbon monoxide is toxic and thus a health hazard; unburned gasoline and oxides in nitrogen can react under favorable conditions to produce eye irritation and to damage vegetation; and smoke from partially burned lube oil can easily restrict visibility and irritate the lungs in enclosed spaces. These are qualitative facts well known to everyone. The importance of exhaust as a contributor to air pollution in a given locality depends, of course, on the qualantitave aspects of the problem.

Let's look first at the nature of motor vehicle exhaust. An automobile engine is unique in that it is called upon to meet many requirements. It must not only produce power; it must produce it in varying amounts, depending on conditions. It must respond rapidly, be easy to start, light in weight, rugged, cheap, and use a high-density fuel. Although combustion efficiency is important, it has naturally been secondary to power production. Accordingly, the variable power requirements of different portions of the operating cycle have resulted in variations in combustion efficiency.

Values for the various important parameters under the four common phases of operation—idle, acceleration, cruising, and deceleration—are shown in Table I.

At *idle,* only enough power is needed to keep the engine running smoothly. The usual air-fuel mixture (11:1 to 12.5:1) is on the *rich side,* compared with the stoichiometric 15.2:1. The engine idles at about 400-500 rpm., or slightly higher in cars with air conditioning and other power-absorbing equipment. The air flow is low (ca. 6 to 8 cfm.) and vacuum in the cylinder is 16-20 in. Hg. Exhaust composition is roughly 500 to 1000 ppm. hydrocarbons; 50 ppm. oxides of nitrogen; and 4% carbon monoxide. The hydrocarbon content amounts to about 5% of the fuel supplied to the cylinder. At the low air flow used, distribution of fuel to the 6 or 8 cylinders is not uniform, so combustion in a given cylinder may vary considerably from the average. Of course, a misfiring spark plug will affect combustion efficiency to a much greater extent than maldistribution.

Under *accelerating* conditions, the flow of both fuel and air is increased markedly, engine speed increases, spark timing is advanced, and combustion conditions continually change. Exhaust composition depends on many factors, such as rate of acceleration, over-all accelerating time, and change in gear ratio. In a typical situation, air flow is 30-35 cfm., air-fuel ratio is 11:1 to 13:1, engine speed goes from 400 rpm. to 3000 or even 4000 rpm. Cylinder vacuum will vary from 0 to 7 in. Hg. Typical exhaust composition is hydrocarbons, 50-500 ppm.; carbon monoxide, very low; oxides of nitrogen, 1000-4000 ppm. The hydrocarbon content represents about 3% of the fuel supplied to the cylinders. The wide range in hydrocarbon value is largely a function of the carburetor-transmission combination. Analyses of exhaust from cars using standard transmission sometimes show only 50 ppm. hydrocarbons. With automatic transmissions, however, much higher values have been found.

Under *cruise* conditions, we again reach a steady state. Air flow varies

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from 15 to 35 cfm., depending on speed. In many modern cars the air-fuel ratio is even on the lean side, or greater than 15.2:1. Cylinder vacuum is normally 7 to 19 in. Hg and combustion efficiency is excellent. Exhaust composition is approximately 200-300 ppm. hydrocarbons; 1000 ppm. oxides of nitrogen; and less than 0.5% carbon monoxide. Unburned fuel in the exhaust is in the neighborhood of 2 to 4% of supplied fuel.

Next we come to *deceleration*, which, like acceleration, is a continually varying condition. The deceleration may be for only a short period of time with a partially closed throttle, *e.g.*, going from 70 mph. down to 60 mph. in the open country; it may be a rapid braking action from a high speed to a complete stop in as short a time as possible. We all know from experience that different traffic situations require different types of deceleration. In the typical Los Angeles traffic pattern, 2 types of deceleration are recognized—a moderate deceleration (30 mph. to 15 mph. in 10 sec.) and a heavy deceleration (30 mph. to 0 mph. in 14 sec.). In the latter case the only fuel reaching the cylinder is that from the idling jet, although drying out of the intake manifold may flash a high momentary vapor concentration into the cylinder. Air flow during deceleration is about the same as idle. Cylinder vacuum rises above 20 in., sometimes as high as 25 in. Combustion efficiency is very poor—anywhere from 20 to 60% of the supplied fuel may pass through the cylinders unburned. Hydrocarbon concentration in the exhaust gas varies from 4000 to 12000 ppm.; carbon monoxide concentration is less than 2%; oxides of nitrogen fall to 50 ppm. Because of the high vacuum in the cylinders unburned lubricating oil is often expelled, resulting in dense blue smoke, particularly from motors with bad rings. It is these tremendous variations in automobile operation that make it difficult to assess the contribution of exhaust gas to air pollution in a given instance. There is such a great difference in the mechanical conditions of any 2 cars that the term *average* car is almost meaningless. In addition to this we must know what portion of the driving time is spent in each of the 4 phases of the operating cycle and how each phase is defined. In this regard, too, the term *average car* can be misleading. The average car in downtown Los Angeles at 10 a.m. on a smoggy day may be far removed from the average of the nearly 3 million cars in the County. It is this situation that makes partial control of a given constituent of auto exhaust unreliable. Occasionally it will be helpful; in other cases its effect would be negligible.

TABLE I
Effect of Engine Operating Conditions on Composition of Auto Exhaust

	Idle	Acceleration	Cruising	Deceleration
Air-fuel ratio	11:1-12.5:1	11:1-13:1	13:1-15:1	11:1-12.5:1
Engine speed (rpm.)	400-500	400-3000	1000-3000	3000-400
Air flow (cfm.)	6-8	30-35	15-35	6-8
Cylinder vacuum (in. Hg)	16-20	0-7	7-19	20-25
Exhaust analysis:				
CO (%)	4	nil	0.5	2
NO (ppm.)	10-50	1000-4000	1000-3000	10-50
Hydrocarbons (ppm.)	500-1000	50-500	200-300	4000-12000
Unburned fuel (% of supplied fuel)	4-6	2-4	2-4	20-60

Smog-Forming Capacity of Auto Exhaust

The greatest drive against auto exhaust as a smog-former stems from the Los Angeles area, where the combination of peculiar meterological conditions and more than 3 million automobiles is largely responsible for the eye-irritating, ozone-containing, vegetation-damaging smog peculiar to the area. There is no longer any doubt that the annoying manifestations of Los Angeles smog are the result of an atmospheric photochemical reaction between nitrogen dioxide and gaseous organic compounds, principally those of an olefinic nature. There are other sources of the organic vapors and oxides of nitrogen in the atmosphere, but only those emitted in auto exhaust have been found in sufficient concentrations or are sufficiently widespread to produce the eye irritation and atmospheric oxidant that plague Los Angeles.

The bill of particulars that forces this conclusion can best be summarized in 3 statements:

(1) The only way one can reproduce the smog manifestations of eye irritation and rapid oxidant formation is by reacting hydrocarbons and nitrogen dioxide in the presence of sunlight or equivalent radiation.

(2) The only places we can find sufficiently high concentrations of both hydrocarbons and oxides of nitrogen to account for the eye irritation and high oxidant noticed in smog are on and adjacent to traffic arteries.

(3) A study of the wind paths in the Los Angeles Basin on smoggy days showed that smog-laden air parcels receive their major share of pollutants from automobile traffic.

There are many other bits of evidence pointing to auto exhaust, but these 3 appear adequate. Furthermore, a similar indictment cannot be made for any other source of pollution.

Two questions commonly put to us are: Is smog of the type formed by the photochemical reaction of auto exhaust prevalent elsewhere? Will it ever be? Certainly no other large metropolitan area has this type of smog as frequently or as severely as Los Angeles. However, as car population increases, other areas with similar meteorological conditions, *e.g.*, San Francisco and San Diego, are experiencing this type of smog more often. At one time it was thought that the topography of Los Angeles (dubbed a tipped soup bowl) was a basic requirement for smog, but this is false. Everything else being equal, the mountains on 3 sides of the Basin are not nearly so important as the combination of prolonged atmospheric inversion, weak winds, and strong sunlight. These are the factors that contribute to the San Francisco and San Diego problems. On occasions, New York and Detroit have experienced this type of smog, but the meteorological conditions conducive to it are present much less frequently than on the West Coast. However, if car population increases sufficiently, more attacks can be expected.

One of the unknown factors in what I call *the photochemical type of*

smog is the effect of sulfur dioxide and smoke. Eye irritation wasn't noticed widely in Los Angeles until these materials were largely removed from the atmosphere. Further, it is reasonable to suspect that sulfur dioxide and an oxidant cannot co-exist in the atmosphere except at very low concentrations. Whether this is related to eye irritation is not known.

Another difference between West Coast smog and that commonly experienced elsewhere is the duration of the attack. In Los Angeles we say the smog *goes away at night.* This is caused partially by increase in wind velocity, but mainly by the setting of the sun and consequent loss of energy to initiate the photochemical reaction. Conversely, in the various air pollution disasters throughout the world the attacks lasted from several days up to a week. There has been some concern in Los Angeles as to the possibility of a week, let us say, with no wind and a strong inversion, during which pollutants could be concentrated to toxic levels. However, if this ever happens, the importance of auto exhaust will be in its carbon monoxide and nitrogen oxide content, and not in the highly reactive ozone formed by a photochemical reaction during daylight hours. Similarly, in most eastern and middle-western cities, the acute auto exhaust problem during a prolonged smog attack is most likely to stem from its carbon monoxide and oxides of nitrogen content. But I suspect that before toxic concentrations of these gases are attained, sulfur dioxide, sulfur trioxide, and plain smoke will have taken their toll. The other effect of auto exhaust, the nuisance of aldehyde odor and irritation in the vicinity of exhaust pipes, is of course a transient and localized problem that can hardly be called smog.

Solving the Auto Exhaust Problem

The solution to the auto exhaust problem depends, of course, on how much and which pollutant one must eliminate. In Los Angeles it has been assumed that either unburned gasoline or nitrogen oxides must be drastically reduced in order to solve the problem. Three approaches have been considered seriously: (1) a fuel-cutoff device on the carburetor, which would operate during deceleration; (2) a nitric oxide eliminator; and (3) an afterburner in the exhaust system to burn residual organics catalytically or by direct flame. Fuel modification has also been proposed, but would be of doubtful value.

There is some doubt that a carburetor device will remove sufficient organics to be worthwhile, so emphasis is being placed on the chemical devices. Currently the stumbling blocks are 3: (1) We need a catalyst that will speed up nitric oxide decomposition or reduction. (2) We need an oxidation catalyst that will not be adversely affected by lead compounds in the exhaust gases. (3) In the noncatalytic field we need a method of burning the organics in exhaust in a reaction chamber small enough to fit under a modern car. Each of these 3 problems is primarily in the field of chemistry and chemical engineering. It is to these disciplines we must look for a solution.

Of course, research and development cost money and the problem won't be adequately tackled unless there is a reasonable hope of financial gain to the one who solves the problem. Thus 2 questions might well be posed: Is there a market for a suitable device? What is the size of the market?

There is definitely a market for nearly 3 million units in the Los Angeles area. The Board of Supervisors of Los Angeles County has said that whenever a practical device is available it will be required by law. The only delay would be the time required for usual legislative processes and the establishment of an adequate inspection system. Inspection of motor vehicles has never been required in California and probably will not be required until the type of device is known and suitable inspection equipment can be developed. But we expect to overcome these hurdles when a device will have been proved effective. Although Los Angeles will probably be the first proving ground for such a device, the rest of Southern California, and possibly the San Francisco Bay Area, will not be far behind. Potential manufacturers will be even more concerned with the likelihood of broader adoption of an exhaust control device. A restricted market on the West Coast would be of interest to a few manufacturers, but a nationwide market would be preferable.

Fortunately a catalytic or direct-flame afterburner will solve the carbon monoxide problem as well as the hydrocarbon problem, so if an afterburner is adopted on the West Coast, further expansion into eastern cities might well follow. If a simple nitric oxide eliminator is the answer, wide geographical aceptance may not follow. In those areas where the local problem is aldehyde stench or smoking tailpipes, less expensive solutions will probably suffice.

I have attempted to bring out in this talk the various factors that will affect the solution of the air pollution problem brought about by motor vehicle exhaust. My own conclusion is that the most promising areas for research are in the development of a lead-insensitive oxidation catalyst, a nitric oxide eliminator, or a small direct-flame afterburner. These are chemical engineering problems. I heartily recommend them to any chemical or chemical engineering research organization looking for projects that offer economic rewards and, at the same time, promote the general welfare.

Developments in Solid Fuel Burning Equipment in Air Pollution Control*

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The evolution of the power boiler from the early type with hand-fired grate to the huge steam generator of today is a story of man's efforts to improve his standard of living through the use of cheaper power in ever increasing quantities. This is particularly true in the United States where the tremendous industrial growth of the Twentieth Century has proceeded hand in hand with the increase in energy consumption. This is illustrated in Fig. 1 which shows the rate of increase in electric energy sales in the United States during the past 30 years. Consumption of electric energy has been doubling about every 10 years.

The boiler units that are being supplied to provide for this increase in electric energy requirements have undergone significant changes in design for better efficiency. There have also been changes that have greatly reduced air pollution; and, in general, our customers demand this kind of a unit. Our industry is increasing its efforts to meet this goal, and even though complete success has not yet been attained, considerable progress has been made. The purpose of this paper is to review some of the specific areas in which progress has taken place.

Efforts to reduce air pollution problems from the use of coal for power generation have been directed along two broad lines: the first has been to reduce the quantity of coal consumed/KWH and the second has been to reduce the quantity of pollutants emitted to the atmosphere for each pound of coal burned.

Coal-fired boiler units have provided the greatest percentage of electric energy in the past, and they will provide increasing percentages in the future.

The efficiency of coal utilization for power generation is shown on Fig. 2.

*Presented at the 50th Annual Meeting of the Air Pollution Control Association, held at St. Louis, Mo., June 2-6, 1957.

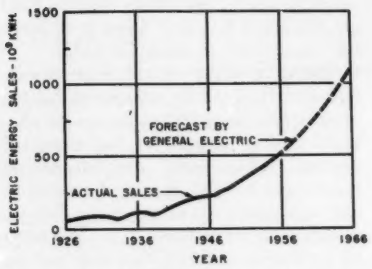


Fig. 1. Annual electric energy sales in the U. S.

During the 10 year period, 1920 to 1930, the coal required/KWH was cut in half, so that the growth of electric energy during this period came with little change in coal requirements. The 10 year periods, 1930 to 1940, and 1940 to 1950, each had reductions on the order of 15 to 20% in coal required per KWH, nevertheless increasing quantities of coal were used to supply the growing demand for electric energy. This trend will continue, but at a lower rate. Our most efficient steam generating unit is the 4500 psi. Supercritical Boiler at Philo Station of Ohio Power Co., which uses 0.65 lb. of coal/KWH. This more efficient utilization of coal has been an important factor in reducing air pollution. However, progress by this means will be at a slower rate in the future, and further gains can only come from reducing the pollutants emitted from the stack with each pound of coal fired.

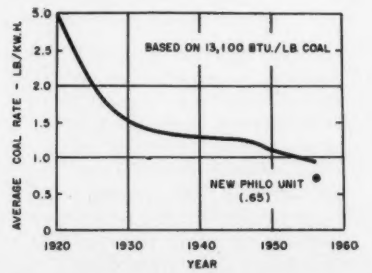


Fig. 2. Efficiency of coal utilization for power generation in U. S.

In designing coal-fired boiler units that will reduce pollution, 3 major results must be obtained:

(1) The volatile portion of the fuel must be burned without smoke.
(2) The solids residue must be retained in the boiler unit.
(3) Obnoxious gases must not be released to the atmosphere.

The realization of these objectives does not rest with the boiler designer alone. Thus, for example, many improvements have been developed in the techniques for pre-treating coal by the supplier and in the efficiency of dust collecting equipment. Here we shall limit our considerations to a review of some of the contributions that the boiler designers have made in alleviating the problem of air pollution.

Combustion of Volatiles

All bituminous coal-fired boiler units can produce smoke, simply by burning coal with insufficient air. The converse is not necessarily true, because if combustion air is not introduced properly smoke can be produced even with considerable amounts of excess air. To obtain smokeless combustion and optimum efficiency, the designer has the problem of burning coal with a minimum amount of air, and this is both a fuel equipment design problem and a boiler design problem.

The basic concepts of fuel burning equipment design have been known for many years. The burner must create a comparatively quiescent zone, rich in fuel, for starting and stabilizing ignition, and it must supply the remaining combustion air in a manner to create high turbulence (mixing). These principles are employed in all types of fuel burning equipment today. However, the effectiveness with which they are now being applied has been acquired

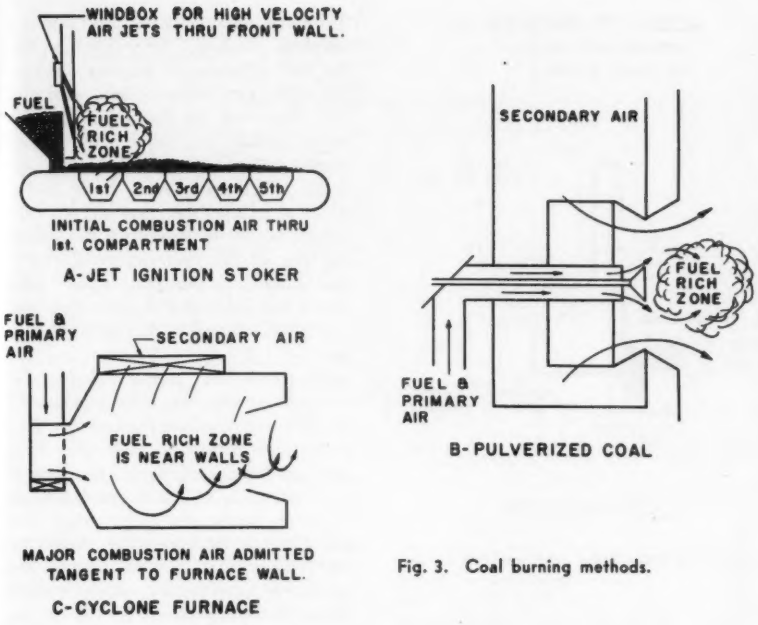


Fig. 3. Coal burning methods.

through many years of experience and continued research. Fig. 3 shows 3 basic types of solid fuel burners employed in today's power boilers.

A shows a stoker with divided air admission compartments. Only a portion of the air passes through the fuel bed as it enters the furnace, thus producing a fuel-rich zone for starting ignition. Combustion of the volatile matter emitted from this zone is obtained by using high velocity over-fire air jets to eliminate smoke and provide the high temperatures necessary for rapid ignition of the incoming coal. The remainder of the combustion air is admitted in the center and rear compartments.

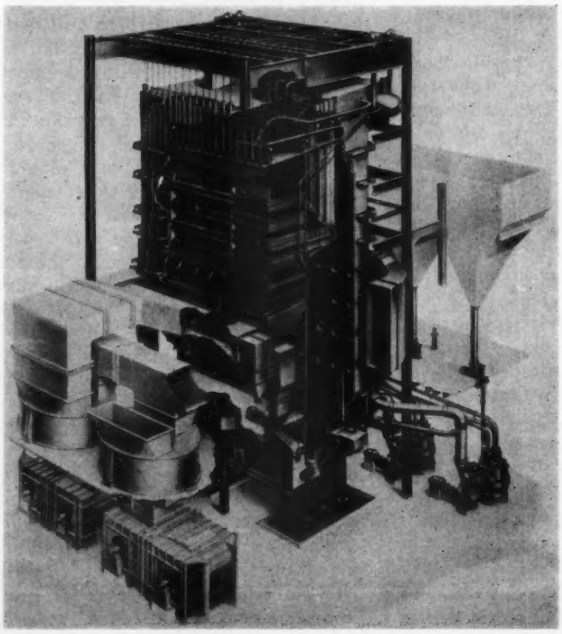
B shows a circular pulverized-coal burner. The fuel-rich mixture is obtained by admitting the coal and primary air at the center of the burner. Secondary air is admitted through the outer annulus in a manner to create the turbulence and mixing necessary for complete combustion.

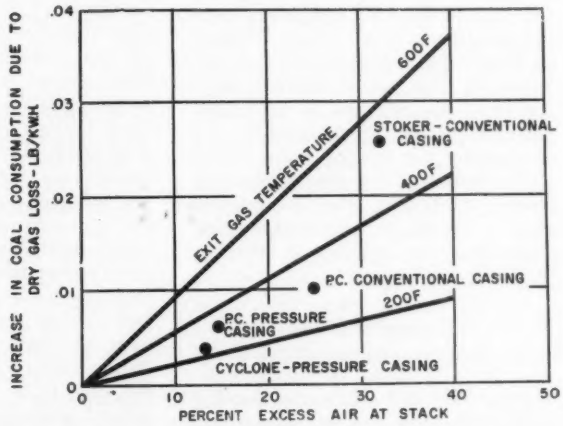
C shows a Cyclone Furnace. Here again, the necessary fuel-rich zone is produced by admitting the coal and primary air at the front of the cyclone. Secondary air is admitted tangentially at high velocity to give the rapid mixing necessary for complete combustion.

These 3 burning devices are examples of how the designer of fuel burning equipment has successfully accomplished the two conflicting requirements of rich fuel-air admission for ignition stability and uniform mixing of fuel and total air for complete combustion with a minimum excess air.

The problem of the boiler designer is to provide a boiler structure with minimum air leakage. Many of our new design boiler units have no air leakage at all, and they are actually operated with the combustion zone and gas passes under pressure. Fig. 4 shows a large utility boiler that operates in this manner. The specially designed pressure casing that makes this possible is already being used extensively on many large utility boilers, and its use is increasing in boilers of all sizes.

The operating level of excess air is one measure of the progress made in burner-boiler design problems. If excess air is reduced, the dry gas loss decreases. This relationship is shown on Fig. 5 in which dry gas loss is ex-





(Left) Fig. 4. Modern pressure-fired boiler steam rate — 1,200,000 lb./hr. Design pressure — 2050 psi. Superheat-1000°F. Reheat-1000°F. 180,000 kw. capability.

(Above) Fig. 5. Increase in coal consumption due to excess air.

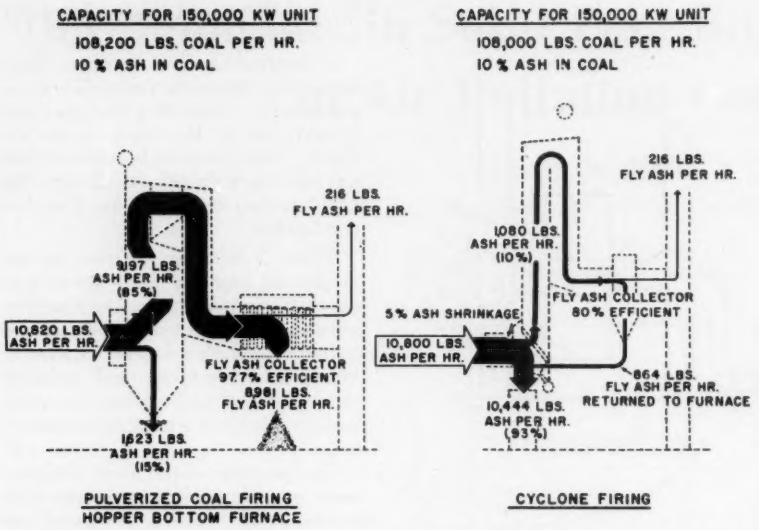


Fig. 6. Typical ash balances for dry ash pulverized coal fired boiler and cyclone furnace boiler.

pressed in terms of the additional coal required when operating above the theoretical minimum quantity of air required for complete combustion. Several different types of boiler units are indicated by points along the curves. It will be seen that the best units closely approach the theoretical minimum. At the same time, developments in automatic controls have made it possible to continuously operate boiler units at low excess air with minimum requirements in manpower.

Progress made in the mixing of coal and air within a minimum space is exemplified by the Cyclone Furnace on Fig. 3 that operates at a heat release rate in excess of 500,000 Btu./ft.^{3}/hr. The problem is no longer one of providing sufficient volume for combustion, but instead is one of providing sufficient furnace wall area to absorb heat from the combustion gases. Therefore, the heat release rate is no longer an adequate criterion of furnace design.

Control of Solids Emission with Flue Gases

The solids in the flue gases leaving boiler units consist of fly ash particles with some unburned carbon. Increasing fuel costs have made it uneconomical to discharge any significant amounts of carbon, so the problem today is essentially to control the ash content of the stack gases. The methods used to eliminate smoke have also reduced the carbon content of the flue gases. With the wide variation in performance of the different burning methods, dust collectors are often required to keep ash discharge within acceptable limits. The Cyclone Furnace has been a significant development in this respect because about 90% of the ash in the fuel is trapped in the cyclone in the form of molten slag. As an illustration of the range of fly-ash loading of flue gases, Fig. 6 shows the ash balance for dry-ash pulverized-coal firing, compared with cyclone-furnace firing. With pulverized-coal firing, 85% of the ash is entrained in the flue gases, whereas, with the cyclone, only 10% of the ash leaves the boiler. To obtain low dust loading at the stack discharge, a dust collector of 97.7% efficiency must be used for the dry-ash unit, whereas an 80% efficient collector is satisfactory for the cyclone. There are also many applications where the cyclones without collectors are giving satisfactory dust loadings.

To summarize the developments in recent years in control of solids content of flue gases: the Cyclone Furnace is a new principle of combustion, resulting in a substantially lower ash content in the flue gases; with other types of firing, ash collecting equipment has been assuming the major responsibility for obtaining clean flue gases, and this trend will continue for the future.

Control of Obnoxious Gases

The control of obnoxious gas as an air pollutant from steam boiler units means primarily the control of sulphur oxides. The sulphur from the fuel appears as sulphur oxides in the flue gases from boilers, and these are dispersed in the atmosphere by high stacks or other conventional means to avoid excessive concentrations at ground level. One method of controlling the amount of these oxides would be to reduce the sulphur content of the fuel before it reaches the boiler, a subject upon which much has been written, but which will not be discussed in detail in this paper.

Progress in boiler design has brought about some new problems in pollution by sulphur oxides. While it is true that more efficient boiler designs have effectively lowered the concentration of smoke and ash particles in stack discharge, they have also tended to lower the boiler exit gas temperatures. These lower temperatures have been causing a visible plume discharge from the stack, particularly in oil-fired units. Investigations conducted at the B&W Research Center indicate that the presence of SO_3 is one of the principal factors involved.

Fig. 7 shows sulphur trioxide concentrations in the flue gases measured at the air heater outlet of several boilers during various firing conditions. These are plotted against the sulphur content of the fuel. No relation between the sulphur trioxide content of the gas and the sulphur content of the fuel is apparent. However, it is evident that up to 40 ppm. (by vol.) of sulphur trioxide in boiler exit flue gases can be expected.

To investigate how this gas might cause a plume, sulphur trioxide was introduced into the exit gases of the small gas-fired furnace shown in Fig. 8. By varying the sulphur trioxide concentration, as well as the temperature of the exit gas, it was possible to produce a visible plume under certain conditions, even though the excess air was constant at the optimum level for best combustion. It was found that concentrations of sulphur trioxide in flue gas as low as 10 ppm. could produce a visible plume. At any given concentration in the flue gas, the amount of visible plume was always substantially greater when the exit flue gas temperature was low. The plume was not visible at all with high exit gas temperatures.

The chemical engineers have an explanation for this because the chemistry of sulphur trioxide is well known, since it is used in the pro-

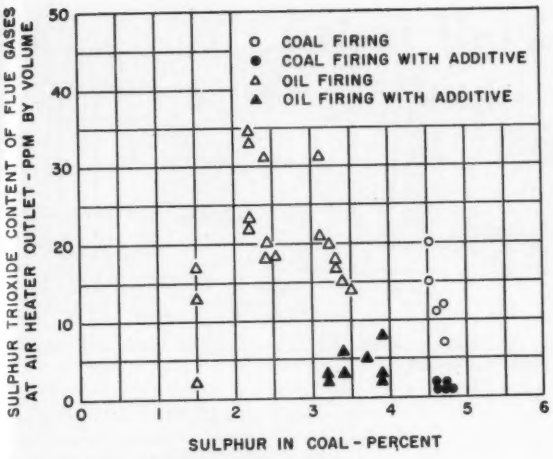


Fig. 7. Sulphur trioxide content of flue gases with various firing conditions.

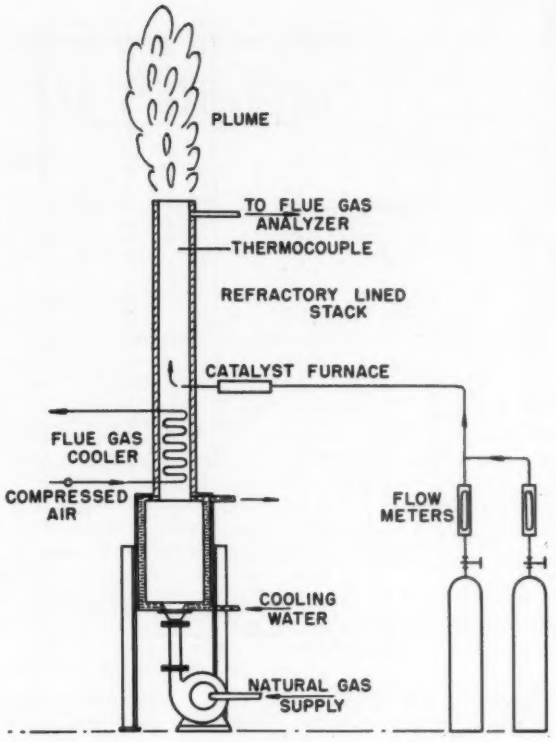


Fig. 8. Laboratory gas fired furnace used for plume studies.

duction of sulphuric acid. Actually, boiler units possess all the elements of a sulphuric acid plant, but fortunately they are poor sulphuric acid producers because optimum conditions for maximum production of acid do not exist. As shown in Fig. 7, some SO_3 is produced that can readily react with water vapor and condense from the flue gases as sulphuric acid. The subsequent corrosion of low temperature metal parts of boilers by this acid is a well known problem in steam boiler equipment.

From the known properties of sulphur trioxide, the conditions under which it will condense from the boiler exit gases to form sulphuric acid can be calculated. Fig. 9 shows the calculated relationship between the rate of mixing of boiler exit flue gases with air and the concentration of condensed sulphur acid vapors caused by the cooling of the flue gas as it is mixed with air. The curves are based on mixing flue gases from oil firing with 70°F. air at 60% relative humidity. Thus, for example, flue gas at a temperature of 300°F. containing 20 ppm. of SO_3 will start to condense when it is cooled by mixing with air in a ratio of 0.2 parts of air to 1 part of flue gas as shown on the curve. Concentration reaches a maximum when 0.6 parts of air are mixed with 1 part of flue gas. The concentration of sulphuric acid is 11.4 ppm. in the mixture at this point, with practically all of the SO_3 having condensed. Subsequent mixing of flue gas with air gradually reduces the concentration of acid by simple dilution.

It is interesting to observe that when the temperature of the flue gas is raised from 300°F. to 400°F., the maximum concentration of condensed acid is reduced.

From these curves it is apparent that the trend in boiler design to lower exit gas temperatures is increasing the concentration of condensed acid in boiler stack gases. The chemical engineers can predict the amount of acid that will be condensed, but not the concentration required to produce a visible plume. Since the small pilot gas furnace used for these tests produced a visible plume at 10 ppm. of SO_3 under conditions similar to those in many boiler units, it is believed that concentration levels in the range of 10 to 30 pp.m. of acid condensed in the mixture of air and flue gas will produce a visible plume.

Referring again to Fig. 7, it will be seen that additions of a basic material, such as dolomite, to the flue gases will reduce SO_3 concentration. This has been demonstrated for both oil and coal firing and indicates that something may be done in the future to reduce the plume problem. However, it also indicates that, as the dust loadings of boiler exit gases are reduced, some of the elements that are now helping to control the formation of plume may be removed, with the result that plume formation may tend to increase. This is particularly true of coal-fired boiler units that handle ash with alkaline characteristics.

The complete removal of all sulphur oxides from flue gases can be accomplished only by a washing method. An example is the installation at Battersea Electric Power Station in London. As described in the literature, the gases are scrubbed with a lime slurry that removes the sulphur oxides as calcium sulphate. This system is not a completely satisfactory solution because it creates some new problems, including disposal of the calcium sulphate, which some people feel are worse than the original problem.

It may be of interest that a similar operation is in commercial use here in the United States. Fig. 10 shows a Magnesium Bisulphite Recovery Boiler, that uses as fuel the waste liquors from cooking wood pulp in the paper-making process. Sulphur compounds are combined with magnesium compounds for producing the cooking liquor used in digesting the wood pulp. The sulphur compounds for this liquor are recovered from the boiler flue gases. One of the main problems of a gas washing plant is solved here—the disposal of the chemicals removed from the flue gas. In recovery units they are recycled to the process. Although the system

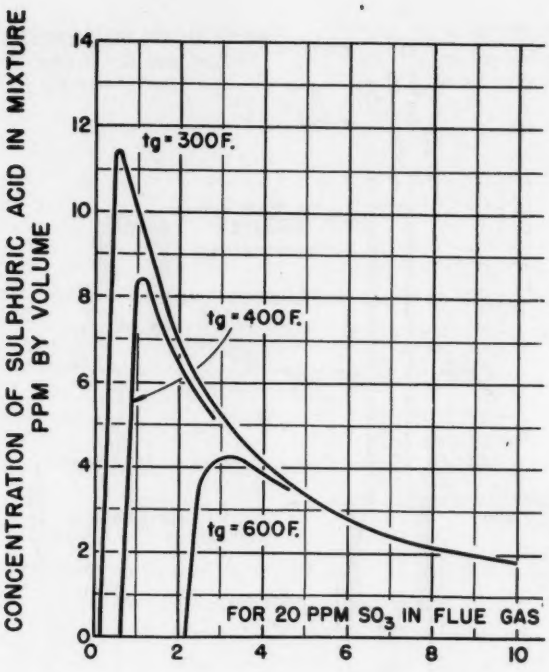


Fig. 9. Concentration of sulphuric acid in flue gases diluted with air. Dilution ratio of mixture = ft.³ air/ft.³ flue gas.

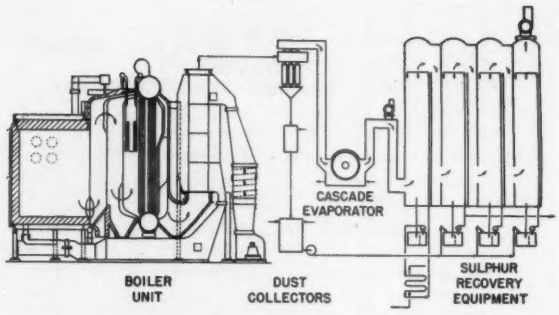


Fig. 10. Magnesium bisulfite recovery system boiler with sulphur removal equipment.

is limited to the paper making process and even to only a few types of paper made in this manner, it does illustrate an economical, commercial application of the technology of gas washing. Four such units are in operation, two in the state of Washington and two in Alaska.

In summarizing the three factors in boiler design that affect the problem of air pollution, considerable improvement has been made during the past 30 years in reducing air pollution by reducing the quantity of coal burned/KWH of electricity. The rate of reduction in the amount of coal burned/KWH will be considerably lower in the future than it has been in the past. Hence, any further substantial reduction in pollution must necessarily come from lowering the amount of pollutants emitted from each pound of coal burned. Considerable progress has been realized in this respect. Developments in fuel burning equipment and boiler design have provided means for completely eliminating smoke. Important reductions in dust emission have been obtained by reducing carbon content of fly ash to a practical minimum. The development of the Cyclone Furnace has afforded a new means of greatly reducing fly-ash emission. For other types of firing, reduction in fly-ash emission has been largely through the use of increasingly efficient dust collectors.

The control of obnoxious gases has become more difficult as advancements in boiler design have been realized. Further research and development is required to determine the best approach for solving this problem.

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A Critical Review of Two Recent Russian Books on Air Pollution*

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New York, New York

This paper contains a critical review of two Russian books: *Sanitary Safeguard of Atmospheric Air*, Moscow, 1954, by Professor V. A. Riazanov, and *Maximum Allowable Concentration of Air Pollutants*, edited by Professor V. A. Riazanov, Moscow, 1955. These books illustrate for the first time the development and trends in the newest branch of hygiene — the hygiene of the atmosphere — in Russia. The contents reflect the tendency of Russian scholars to follow an isolated path.

The most important point of these books is the official announcement about the introduction of maximum allowable concentrations of atmospheric pollutants.

Is this step essentially useful? Is there sufficient substantiation for each limit set for individual pollutants? What of the difference between hygienic and technological limits? Is it possible to find an interrelation without disregarding one of them?

This critical review attempts to answer these questions.

The book *Sanitary Safeguard of Atmospheric Air* refers to problems of air pollution and purification in a summarized form, ranging from such questions as the theory of air pollution, toxicology and physiology and including the technology of some industrial processes that represent sources of air pollution. The paper also deals with the principles of hygienic standards that must be established for atmospheric pollutants.

In the chapter about the planning of cities we find a description of restricted zones (zonarazryva). The conclusion of the book is devoted to the organization of work for the sanitary safeguard of atmospheric air.

The book *Maximum Allowable Concentrations of Atmospheric Pollutants* reports on the *second stage of work done by the Commission for Maximum Allowable Concentration of Atmospheric Pollutants* and on methods which are applied to determine atmospheric pollutants.

Problems of Air Pollution Control from the Viewpoint of Pavlov's Teachings

Certain sections of the book are characterized by an attempt to approach the essential problem of the hygiene of the atmospheric air from the viewpoint of Pavlov's physiology. The studies on central nervous system activity by I. P. Pavlov are currently popular in the field of Soviet hygiene.

According to author of these books, Professor V. A. Riazanov, a "reorganization of hygiene in the light of Pavlov's teachings" was launched 7 years ago and is still in the process of development. Professor V. A. Riazanov is a pioneer favoring the new trend of hygiene.

Ever since this "reorganization" of hygiene on the basis of Pavlov's teachings was begun, no satisfactory answer has been found to the essential question: how can the defense reactions of the organism to the action of harmful substances be evaluated?

At the time when hygienic limits were worked out and established, some research was conducted with a view to applying and testing physiological methods and methods of conditioned reflexes. But all this research did not adequately clarify the issue of the maximum allowable concentration of contaminants in atmospheric air. Professor M. K. Petrova's research deserves attention in which she emphasizes the role of the central nervous system in the formation of malignant neoplasm.[12] M. K. Petrova proves that in addition to the direct influence of cancerogenic substances, the lowering of the body resistance also contributes to the formation of cancer. She claims that this is the result of an interrupted normal activity of the cerebral cortex.[12]

Some papers were published recently on different kinds of pollutants and discussing the application of physiological methods.[1]

Maximum Permissible Concentration of Pollutants in Atmospheric Air

Now comes the crux of the matter —the establishment of the maximum allowable concentration for air pollution.

First, it is necessary to study the definition "concentration" as understood by Riazanov. The Special Commission headed by him recommended as a basis an average daily concentration to determine the degree of pollution, while it suggested an additional limit on the basis of a single maximum exposure should be established for substances characterized by odor, irritation of the respiratory passages or of the mucous membrane of the eyes and which may cause serious intoxication in concentrations that may actually exist.

At this point, the author tried to establish a correlation between the average daily concentration and the maximum single exposure.

The available data testify to the fact that most frequently average daily concentrations are in a 1:3 relation to maximum single exposures during the same day.

Here are some principles of setting hygienic limits for atmospheric pollution.

> "We are only interested in the threshold of the olfactory and irritating reaction inasmuch as it is below the threshold of the basic effect of the given poison. For that reason we should not reject those persons who volunteer to be subjected to tests."

Along with laboratory tests designed to determine the threshold of the olfactory and irritating effect of atmospheric pollution, tests are fre-

* Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

quently conducted by questioning the population that lives at different distances from the source of pollution. Professor Riazanov indicates correctly that the latter method reveals that the threshold is much lower than in tests conducted under laboratory conditions. He reminds also that in view of the extreme variability of the concentration in atmospheric air, we usually fail to get the peak concentration. As a rule, our data are more based on an average. To determine an odor, however, one has only to inhale—in other words, it takes 1 to 2 sec.

> "Consequently, a human being can instantaneously determine a concentration by inhaling which cannot be determined at a later time since our methods are not adequate in this respect. These facts cast certain doubts on the method of making a study of the population by questioning and lead us to assume that the real threshold is higher than indicated by the result of such a survey."

Now it is important to mention here what is known as the adaptability to poisons. "The habit-forming that develops as a stable phenomenon upon the chronic influence of poisonous substances is clearly pathological. It not only serves as a reason to reduce hygienic requirements but, on the contrary, should be considered as a factor which would raise the hygienic requirements when limits are established. Along with a chronic formation of habits, hygienists and physiologists are very familiar with the adaptability to the strong influence of smells. But does it mean that the harmful effect has ceased too? Of course it does not. The poison continues to affect the body without signalling it to the cerebral cortex. For that reason, the adaptability becomes an unfavorable factor eliminating the signalling action of the smell."

Later we find the following state ments: "In addition to the direct effect of air polluting matter on man, it is necessary to consider its indirect effect. Concentrations of smoke that reduce markedly visibility, light in dwellings, the biological effect of ultra violet radiation, increase fogs, *etc.*, should not be allowed since these factors, in turn, have an unfavorable effect on health.

> "The only proper approach to a total evaluation of the harmful action of a specific pollutant of the atmospheric air is resorting to the principle of the *vulnerable point* [italics belong to the author of the paper]. In other words, the limits must be set according to the most sensitive index. If one gas or another could be detected at concentrations considerably below those that impair human and animal life in any way — regardless of whether the effect is acute or chronic, direct or indirect — the limits should be established according to the threshold of sensory perception. In those cases when a substance that enters the atmosphere has no odor, no irritating effect on mucous membranes and no harmful influence on plant life in concentrations which do, nevertheless, have a toxic effect on human beings, the limits have to be established according to the threshold of toxic effect.
>
> If the vulnerable aspect of a substance were its harmful effect on plant life, the threshold of its action upon vegetation should be considered in the elaboration of limits."

In principle it must be agreed that it is necessary to establish limits for the purity of atmospheric air. But the question as to the elements for which limits have to be established and in which manner this should be accomplished has, so far, not been solved satisfactorily.

At the present stage of development of biochemistry and medicine, the justification for maximum allowable concentrations of individual pollutants is inadequate. Therefore, it is considered premature to set limits at present. Nevertheless, limits must be adopted in principle. They must be set as a goal which has to be achieved. However, they can only be formally established after a thorough and scientific substantiation is found for them.

In order to establish the degree of contamination of atmospheric air it must, of course, be possible to compare the actual concentration with its allowable maximum. It is necessary to have a standard of measurement. Riazanov feels that a further advantage of limits is that they help to establish the efficiency of control devices, set restricted zones (the distance between the source of pollution and a populated area), *etc.* This is not, however, the principal advantage of established limits. They may serve as a scientific basis for the hygiene of atmospheric air. Without a scientific foundation the hygiene of atmospheric air cannot develop and progress properly.

The tremendous technical progress places increasing demands before the hygiene of atmospheric air. It is necessary to study the combined effect of air pollutants on the one hand, to investigate new pollutants which emerge as a result of using new substances and new processes, on the other. It is also imperative to study their effect upon health.

All these arguments make the idea of having established limits a goal that cannot actually be attained. This very fact is a guarantee that the hygiene of atmospheric air will never cease to exist as a science forever striving to attain this goal.

In terms of Pavlov's teachings we may state that limits may become the constant minimum irritants which are necessary to maintain the hygiene of atmospheric air in a state of activity.

The work of various authors on maximum allowable concentrations reveal that they resort mostly to industrial toxicological data in their arguments. Present industrial norms are amplified by additional information available from literature and from individual conclusions. For that reason, the adduced substantiations are not convincing. There is, however, one exception: the substantiations in favor of limits for dust on the basis of Richter's paper *Correlation between the Transparence of Atmospheric Air and its Dust Content.* We shall discuss this paper separately.

Even Professor Riazanov has to admit that norms are inadequately substantiated. After the Congress of Hygienists in June 1956 in Moscow, the editor of the journal *Gigiena i Sanitarija* [Hygiene and Sanitation] Professor Riazanov stated:

> "Originally established hygienic standards which were frequently based on obsolete ideas and primitive methods evoke natural doubts as to their objective accuracy. The need arises to review hygienic standards on the basis of the current state of medical science and modern methods of research."

Examining the occurrences in Donora, London and other areas it can be affirmed with certainty that it was not possible to establish definitely that one certain pollutant had caused the disaster in any of the cases.[3] It is

always possible that another pollutant or the combination of several pollutants had ill effects. Sulfur dioxide in urban air means only that the air is polluted, but that is about all.

It is quite likely that meteorological conditions were the main and, perhaps, the sole reason for a sharp increase in SO_2 and H_2SO_4 concentrations.* As a rule, the average daily concentration in London during the month of December is 0.35 mg./m.^{3} of air. The day before the disaster of December 4 the average daily concentration amounted to 0.378 mg./m.^{3} and the peak concentration reached 1.34 ppm. or 3.5 mg./m.^{3} Meteorological conditions similar to those in London could also lead to unfavorable effects upsetting Professor Riazanov's limits of 0.25 mg./m.^{3} as a maximum daily concentration of SO_2 and 0.75 mg./m.^{3} of air as his single peak concentration.

According to Mary Amdur and other research in this field toxicity of sulfuric acid exceeds that of sulfur dioxide 5 times.[2] It is important to emphasize that sulfuric acid is always found as an aerosol while sulfur dioxide is encountered in the form of gas. Sulfur dioxide, for instance, "if borne in or on particles of about 0.2 μ diam." might reach the deeper tissues up to 5 times more — as already pointed out—than if it were inhaled in the form of gas.[3]

By way of example we should also like to refer to hydrogen fluoride which, in combination with beryllium, increases the lethal effect when inhaled by animals although individually neither the former nor the latter are lethal.**

Professor Riazanov made ample use of literature when he worked on the maximum allowable limits for SO_2 concentrations in atmospheric air. He based his work on Thomas' and Hill's paper and research who used the intensive photosynthetic activity (establishing the acute effect of sulfur dioxide on the process of assimilation in plants sensitive to this gas) as a symptom of the harmful action of sulfur dioxide. The changes in workers discovered by Keche, Michael, *et al.* may be interpreted as a result of the chronic effect of minor concentrations of sulfur dioxide but they were observed with concentrations considerably above the threshold of irritation. In this regard Professor Riazanov regrets that "no protracted observations dealing with the effect of minor concentrations of sulfur dioxide on persons exposed to it continuously for 24 hr. have even been completed."

At this point it should, however, be mentioned that Amdur and others conducted a series of extremely interesting tests (in 1952) exposing subjects to various concentrations of SO_2 and H_2SO_4.[2, 3] These concentrations were introduced at levels below that of the threshold of detection. The subject had no knowledge of inhaling toxic air. At the same time their heart and respiratory pattern as well as the respiratory volume were studied. The physiological changes produced in the subjects testify to the fact that they are entirely natural reflexes. "We may see from the diagrams that there is a great difference between the toxic action at short exposures and after long exposures. It is of interest that workers who have acquired a habituation to sulfur dioxide did not show such reflex changes."[4]

Let us turn now to lead, another toxic material frequently encountered in the air. We shall show now how the limits for this pollutant were founded.

> "First, a certain preliminary estimate should be made based on a survey of the toxic nature of lead introduced through drinking water. We know that concentrations of 0.35 mg./*l.* and more are dangerous when the water is regularly used. Maximum allowable concentrations of lead in drinking water are 0.1 mg./*l.* that means 0.2 mg./day. If we acted under the assumption that human beings inhale 15 m.^{3} of air within 24 hr. — the toxic effect of lead being analogous whether inhaled or absorbed through enteric introduction — the safe concentration of lead in the air would be 0.013 mg./m.^{3} It is, however, generally known that inhaling lead is more effective than its oral introduction since lead penetrates blood channels directly from the lungs bypassing the hepatic barrier. For that reason the tentative concentration (0.013 mg./m.^{3}) would have to be reduced by at least 20 times, *i.e.* to 0.65 γ/m.^{3}***

H. M. Tomson's observation may be used to substantiate the maximum allowable concentrations. The scholar kept test animals for long periods of time in cages at various distances from the plant that was the source of lead pollution. We see that according to both, H. M. Tomson cording to both, N. M. Tomson and Right, a concentration of 6 to 7 is still effective. In view of the fact that the average human being (including old people, children, weak and ill persons, *etc.*) reveals a greater sensitivity to lead than industrial workers who have probably acquired a habituation, this threshold concentration should be reduced by several times. For that reason, the maximum average allowable concentration of lead in the atmospheric air approved by the All-Union State Sanitary Commission does not exceed 0.7 γ/m.^{3} and it should be considered safe."

Technological Limits of Maximum Permissible Emission for Different Productions

As it is impossible to elaborate substantiated limits under the present conditions, our attention is focused on technological limits which thus acquire greater significance.

Although the concentration of pollutants in the flue does not necessarily show the concentration in the zone of inhalation — this according to Professor Riazanov — we may add that neither does the concentration of pollutants in the zone of inhalation reveal the concentration of pollutants in the flue. We refer here to industrial centers and major cities, in particular, where the influence of the background may be very prominent. Professor Riazanov goes along here, too.

The intensity of the background may be judged by conditions that prevail in a city like New York.[6, 7] There is no doubt that a background has formed here which — in addition to local sources of contamination — is continuously supported by massive industrial pollution in New Jersey.

There is no practical possibility of checking the allowable emission of each individual enterprise on the basis of hygienic standards — even if we assumed that these standards— were well grounded. For that reason, it is rather difficult to determine zonal contamination with a view to

* The Maximum Allowable Concentration Value of SO_2 is 10 ppm. Lethal values approximately amount to 100 ppm.

** The recent Poza Rica incident of November 1950.

*** $\gamma = \frac{1}{1000}$ mg./m.^{3}.

their individual sources in large cities and industrial centers. It should be emphasized that many other factors are involved in defining the degree of pollution:

(1) the method of selecting air samples;
(2) the sensitivity of a given method of analysis;
(3) the length of sampling time;
(4) number of samples taken to determine the average concentration.
(5) distance between the point where air samples are taken and the source of emission.

In addition to the volume and height of emission (absolute quantity of pollutants) the following elements also affect the volume of concentration when it comes to establishing it at a certain point of the source:

(1) frequency with which samples are taken at a certain point of the plume; and
(2) direction and velocity of the wind.

The direction of the wind which changes frequently leads to errors in determining the *smoke rose* that serves as the basis for average daily concentration. Mr. Riazanov states in reference to this fact:

"The actual picture can be obtained by selecting air samples with a device that would be set in motion automatically (with the help of a weathercock) in the direction of the wind but also would shut off automatically as soon as the wind changes direction."

If we would still add that the concentration of pollutants depends also on vertical temperature gradient, on the relative humidity of the air, and on self-purification of atmosphere it would be evident how variable is the concentration of pollutants in the atmospheric air; in other words, how difficult it is to be determined absolutely.

It is necessary to turn our attention to the source of emission, for correct and full comparison of hygienic and technological limits (ground concentrations of pollutants and concentrations of pollutants in the stack).

However, while technological norms are worked out it must be considered, as Professor Riazanov states correctly, that the concentration of both sulfur dioxide and ashes in the atmospheric air determine the absolute emission from the stack and not their concentration in flue gases. It goes without saying that the types of fuel and the techniques of burning is of tremendous significance for the pollution of atmospheric air with ashes and sulfur dioxide. The concentration of sulfur dioxide in flue gases is more significant when it comes to purifying flue gases. The more concentrated the gases the easier the purification process.

In order to avoid the miscalculations it is necessary to emphasize that the emission/1 kg. of fuel does not represent a complete picture of the sanitary harm of a given kind of fuel. The point is that, in order to obtain an equal quantity of electric energy (power) or steam, the amount of fuel used increases in proportion with its decreasing heat value. It happens occasionally that fuel that produces a greater value of emission/1 kg. has a smaller emission/unit of the capacity (power), generated by the plant. It is, therefore, obvious that in order to evaluate properly the qualities of the fuel from a sanitary point of view the emission of sulfur dioxide/ton of an ideal fuel with caloric value of 7000 kcal. should be determined.

It is also important to remember that by shifting to low grade fuel the higher emission of ashes is not only caused by the greater amount of ashes that is carried out/1 kg. of fuel but also by an increased use of fuel, as a result of its lower calorie content.

Knowing the emission of ashes/1 kg. of fuel, its caloric value and the coefficient of the excess air it is easy to figure out the concentration of ashes in flue gases with various types of fuel and different techniques of burning the fuel.

Professor Riazanov quotes the results of analyses of dust concentration in the air near large modern power plants that do not have dust collectors. The following data show the concentration of dust in the atmospheric air near one of the largest power plants emitting 500 tons of ashes in 24 hr. into the atmosphere.

Distance in m.	Maximum single concentration in mg./m.³
250	29.3-79.0
500	9.6-63.4
1000	2.2-39.4
2000	0.5-33.5
3000	0.2-18.0

According to the research conducted near one large heat and power generating plant, which emitted 280-360 tons of sulfur dioxide in 24 hr., the concentration of sulfur dioxide fluctuated from leeward side as follows:

Distance in km.	Concentration of sulfur dioxide in mg./m.³	
	From-To	Average
0.2-0.5	0.30-4.90	3.00
0.5-1.0	0.70-5.50	2.70
1.0-2.0	0.22-2.80	1.60

Professor Riazanov concludes.

"Obviously the concentration of sulfur dioxide in the atmospheric air of modern cities is extremely high. This applies particularly to areas near large power plants and boiler installations where concentrations exceed the

TABLE I

Threshold Industrial Limit Values
(in mg./m.³)

No.	Name of contaminant	Chemical formula	U.S.A. 1956	U.S.S.R.	U.S.S.R. Single sample	A P limits Daily average
1.	Manganese and its compounds	MnO_2	6	0.3	0.03	0.01
2.	Nitrogen penta-oxide	N_2O5	—	5.0	0.5	0.15
3.	Carbon Monoxide	CO	100	—	6.0	2.0
4.	Mercury metallic	Hg	0.1	0.01	—	0.0003
5.	Soot	—	—	—	0.15	0.05
6.	Dust non-toxic	—	—	—	0.5	0.15
7.	Lead and its compounds	Pb	0.15	0.013	—	0.0007
8.	Sulphur dioxide	SO_2	25.00	20.00	0.75	0.25
9.	Sulfuric Acid	H_2SO_4	1.00	0.5-2.0	0.30	0.10
10.	Hydrogen Sulfide	H_2S	30.00	—	0.05	0.015
11.	Carbon Bisulfide	CS_2	60.00	10.00	0.5	0.15
12.	Arsenic compounds (inorganic)	As	0.5	0.3	—	0.003
13.	Phenol	C_6H_5OH	19.0	5.0	0.05	0.015
14.	Phosphorus penta-oxide	P_2O_5	—	1.0	0.15	0.05
15.	Fluorine compounds	F	0.2	1.0	0.03	0.01
16.	Chlorine	CL	3.0	1.0	0.10	0.03
17.	Benzol	C_6H_6	110.0	50.0	—	—

permissible limits from a hygienic point of view by many times; a safe level cannot be achieved for the time being, since experience in removing sulfur dioxide from flue gases has not proved adequate as yet."

With the help of suitable mathematical formulas it would be possible to find a correlation between concentrations pertaining to the zone of human respiration and the concentrations in the stack. This formula could establish the expected concentration on any given distance from the source of pollution. In spite of the absence of a proper formula it is still possible, utilizing some of the existing formulas *(Sutton)* to determine the concentration for normal meteorological conditions, but unfortunately these formulas are not suitable for meteorological conditions such as temperature inversion, calm, *etc.*

Summing up the above we are led to conclude that for an accurate determination of the degree of contamination of atmospheric air it is necessary: *(1)* to consider the influence of the background thoroughly; and *(2)* to establish technological as well as hygienic limits.

Here is the opinion of Professor Riazanov in regard to the technological limits:

"Technological limits should not be used as a basis for sanitary practice inasmuch as they do not consider peculiarities of local conditions from a hygienic point of view. Technological limits should be considered as an additional criterion that may acquire significance only if it guarantees the observance of hygienic standards."

At this point it is rather interesting to study the views expounded by Professor R. A. Babaniats (1948).[8]

"The study of the zone unfit for residence around the enterprise requires that an investigation be made as to the degree to which air is polluted at a previously established distance in comparison to the degree of pollution of the air that is as control (areas with relatively pure air). To this end the *gravimetrical* (weight) quantity of aerosols does not necessarily have to be known. In the following 5 to 6 years the admissible concentration of dust for our industrial cities and in view of the present level of technical possibilities to combat the pollution of atmospheric air should amount to 2 mg./m.^{3} (average during the summer)."

When Professor Babaniats speaks of technical possibilities, he has, apparently, in view chiefly the improvement the efficiency of the air cleaning devices. In conjunction with the above we should always keep in mind the improvements achieved during the last years in the design of the boiler and other heat generating installations. The improvement of the efficiency (the increase of useful power/lb. of coal consumed) in such installations has as direct result the decrease of the emission of pollutants from the stacks. The tabulation below,[10] which illustrates this progress, is especially noticeable during the last 5 years.

This indicates an obvious connection between economic factors and problem of air pollution. In the majority of cases a successful solution of such problems will have a beneficial economic aftereffect, which is undeniable in respect to power and heat plants.

Year	Lb. of Coal/ Kilowatt-hour of Electric Energy
1900	7.0
1940	1.34
1950	1.25
New plants	0.75

Concluding the question on maximum allowable concentrations, the methods used to establish the dust contents of the air must be mentioned. Professor Riazanov, for instance, does not favor konometric methods (measuring the number of particles/unit of volume). "Research conducted to determine the dust content in atmospheric air by konometric investigation gives an improper picture of the hygienic value of dusty air. The harmful effect of dust is proportional to the mass of dust that penetrates the organism and not the number of particles." From hygienic viewpoint it is important, therefore, to determine not only the gravimetric concentration (concentration by weight in mg./m.^{3}) in measuring the dust but also its *dispersion* (particles distribution) (italics belong to the author of the paper). Mr. Riazanov concludes: "A further improvement of these standards does not mean that gravimetrical limits have to be substituted for quantitative ones. It is important to replace gravimetrical limits that do not take into account the dispersity of dust by limits that incorporate dispersion." In other words, maximum allowable concentrations of dust in the air must be expressed in terms of mg./m.^{3} of air for various fractions of dust (size of dust particles). This, however, is far from being investigated thoroughly. Nevertheless, Mr. Riazanov hopes that the science of hygiene will cope with this task.

The method of sedimentation which is considered a *classic method* of testing atmospheric air outside of USSR was the target of sharp attacks on the part of Professor Riazanov.[11] This statement is not quite accurate. Many important investigations in Soviet Union were conducted with the help of the sedimentation method of sampling. The main objections against the method of sedimentation are as follows:

(1) A correlation between its data and the concentration of dust in the air is far from always being observed.

(2) The method of sedimenta- does not allow to evaluate the actual degree of air pollution; also its manifestations do not make it possible to evaluate its influence on human organism because human beings are under the influence of the effect of suspended particles and not of those that settled on the ground.

We cannot fully agree with the above statement. Sediments gathered by way of sedimentation contain coarse particles of dust. If it were assumed that the hygienic significance of dust depends primarily on the mass of dust that penetrates the organism (Mr. Riazanov goes along here, too) and that this dependence is a proportional one, the coarse particles of dust represent in some cases more interest than the fine dust from the hygienic point of view.[9, 10]

In addition, settled dust cannot ust be ignored when it comes to determining the concentration.

Do we actually consider that with the method of aspiration not all fractions of dust will be fully represented in the state of suspension and, therefore, the estimation of the mass of dust that may enter the organism will not be accurate? Fractions contained in settled dust may be absent here. However, before settling this dust was suspended and therefore capable of impairing human health to some extent. The problem of the dispersion (particle size distribution) of atmos-

pheric dust needs *further research since materials available on the subject are completely inadequate; there are, for instance, no data on the change of dispersion in accordance with altitude, etc.*,—to quote a passage from the book. The fact must also be considered that settled dust may rise into the air again through the wind. Therefore, besides the influence of meteorological conditions it is an extremely difficult task to search for correlation between suspended and settled dust. The exclusive use of the aspiration method does not provide the actual picture of concentration.

Planning

The proper planning of cities, as Professor Riazanov states, have a great significance in the abatement of dust in the air of populated centers.

This applies primarily to dividing urban territories into populated and industrial districts and establishing an adequately wide restricted area between the two whereby the industrial district should be located at the lee side of the housing district.

The establishment of *restricted zones* (zony razryva), as we shall call them, deserves particular attention. These zones are established in USSR according to the *Sanitary Norms for Planning Industrial Enterprises* (NSP 101-51) approved by the Council of Ministers of the USSR on January 6, 1951. According to these regulations the *restricted zones* are established in each specific case according to the nature of the enterprise. All enterprises are divided in 5 grades depending on the degree of harmfulness of their emissions. A restricted zone of 1000 m. (first grade) has to be established for the most harmful emissions, the least harmful one calls for a zone 50 m. (V grade). *Restricted zones* in very large enterprises should be established individually according to the decision of the All-Union State Sanitary Control. Where no ash collected installations are available or the cleaning efficiency is less than 50%, the *restricted zone* may be expanded by the organs of the All-Union State Sanitary Control but not more than twice. For heat and power generating plants in populated areas the restricted zone is established individually by the organs of the State Sanitary Control, according to the actual situation. Here, particularly when it comes to the restoration or reconstruction of the heat and power generating plant restricted zones have to be reduced in comparison with the norms, stipulated in NSP 101-51. Such reduction of the restricted zone must be compensated by greater demands upon the effectiveness of the ash-collecting installation.

Boiler plants for heating purposes in the vicinity of housing areas with a capacity of 3 tons/hr. (coal or peat) should be separated from the populated area by a zone of vegetations at least 50 m. wide. The height of the stacks for these boiler plants should be 10 m. higher than the tallest building within a radius of 100 m. Boilers with a capacity of 2 tons/hr. should have stacks at least 20 m., and those using 30 tons/hr. should be provided with stacks at least 30 m. high. In accordance with the type of fuel used, the stacks for industrial and power plants should range from 30 to 120 m.

Classification of Aerodispersion Systems

One must recognize that the Professor's call for the establishment of the correct classification is very timely; and by this the necessary clearness will be brought about into this question. Mr. Riazanov believes that the following classification is correct reflecting the physico-chemical properties and hygienic significance of the phenomena involved:

"The general collective term, according to this classification is *aerodispersion, i.e.* a system that comprises suspended particles."

According to the size of the particles aerodispersion systems are subdivided into 2 categories: aerosols with the size of the particles less than 0.1 to 10μ to fine aerosuspensions. size of the particles exceed 0.1 μ. Aerosols are subdivided in smokes; *i.e.* systems with a solid dispersed phase, fogs — system with a liquid phase. Aerosuspensions, in turn, are subdivided into 2 sub-groups, depending on the degree of dispersion (particles size distribution): systems with particles over 10 μ belong to the category of coarse aerosuspensions and systems with particles ranging from 0.1 to 10 μ to fine areosuspensions. Each of these sub-groups is, in turn, divided into systems with a solid despersed phase and a liquid phase.

All aerodispersion systems with a solid phase are known under the general term *dust*. Thus, we have 6 aerodispersion systems:

(1) Aerosol with liquid phase (fog).
(2) Aerosol with solid phase (smoke).
(3) Aerosuspension with solid phase and particles <10 μ (fine dust).
(4) Aerosuspension with solid phase and particles <10 μ (coarse dust).
(5) Aerosuspension with liquid phase and particles size <10 μ.
(6) Aerosuspension with liquid phase and particles size <10 μ.

Problems of Air Pollution and New Ways to Solve Them

Problems of atmospheric air pollution are associated with the chronic effect of small concentrations; this fact represents great difficulties particularly when limits have to be established and substantiated. Other difficulties are caused by the choice of the right method. According to Z. I. Izraelson investigators are familiar with the difficulties that arise when it comes to shifting from an established minimum (on hand of tests with animals) effective value to a harmless and ineffective value and how complicated it is at times to determine the threshold of toxic action. It is even hard to choose a proper criterium of toxicity.[13]

Our hygienists as well as Russian hygienists are fully aware of all these difficulties and are searching for proper ways to solve the basic tasks of air pollution control.

In the light of the above statement Dr. Norton Nelson's comment on M. O. Amdur's studies (which were mentioned above) is of considerable interest:[4]

> "This work emphasizes a point of view of the greatest importance in considering the toxicity of air pollutants; that is, the necessity of giving consideration to functional changes as contrasted with organic changes.
>
> "The functional operation of an organism may be distorted or modified by a toxin without leaving any evidence of trauma if the insult is survived. This suggests the usefulness of searching for such functional changes in the human being and indicates a deficiency in the confenctional toxicological approach based on death or morphological changes in tissues."

Dr. Frank Princi states:[14]

Although the respiratory tract is the obvious portal of entry to the body of atmospheric pollutants, many toxic materials may be absorbed through the respiratory system without providing direct irritation to the pulmonary epithelium: they may exert their primary physiological effect on other organ systems and the individual may still die a cardio-respiratory death.

Therefore, in any consideration of the public health aspects of air pollution, it becomes necessary to consider not only the environment but man's ability to live in such environment.

Consequently, investigations must be directed not only to the study of the effects of air contaminants on the various organs of the body but on the individual as a whole, ensuring its capacity to handle various stresses.

In Professor Riazanov's book we find the following statement which could be applied to this question:

"Tests with animals do not provide a fully satisfactory answer about maximum allowable concentrations. First of all, epidemiological principles may be applied to the study of the state of the population that lives at different distances from the source of pollution.

"The relation between the rate of disease and the purity of the air may be considered as proved if the rate of disease increased in different areas with the same consistency as the increasing rate of the concentration of pollutants; these results being obtained for the entire population of the given and not only for the part that is employed in industry, and confirmed by the age-groups in which the disease occurs."

Evidently, these will be the lines which the hygiene of atmospheric air will have to follow but it is hard to predict how far it will go in this direction. At any rate, judged by what has been accomplished so far it is bound to be successful on this path.

Organization of Work for the Sanitary Safeguard of Atmospheric Air

According to the Sanitary Code of the Soviet Union no new plant may be planned without being equipped with installations designed to purify atmospheric emissions. Neither can any plant be set into operation without a permit from the organs of the State Sanitary Control, which makes sure that the plant is duly equipped with purifying installations.

If purification installations are ready, the State Sanitary Inspectors approve their preliminary use under condition that the enterprise would engage experts to test the effectiveness of these installations. A final approval is issued after the efficiency of purifying installations has undergone expert study. It is up to the technical organization to determine the efficiency of purification but it is the task of the State Sanitary Inspector to organize through appropriate sanitary and epidemiological authorities. A study of the air in the populated center near the new plant to determine whether the purification of emitted gases is adequate. It is desirable to make a survey of the population near the plant to make sure whether the emissions of the plant cause any inconvenience. On the basis of the data obtained the necessary measures should be taken to eliminate any shortcomings.

The control of newly built enterprises is only a part of the tasks of the State Sanitary Inspector to protect the cleanliness of atmospheric air. There are enterprises constructed before the sanitary regulations have been effective. Appropriate health measures must also be carried out in these enterprises and it is up to the State Sanitary Inspector to make sure that this is being done.

First of all, a complete list of all plants, shops and aggregates that serve as a source of air pollution should be prepared. It should also be specified for each of the enterprises what kind of contaminants its emission contain, determining their chemical composition and their volume. On the basis of these materials, lists of enterprises are prepared that must install cleaning equipment.

The State Sanitary Inspector must work with the cooperation of the sanitary-epidemiological centers establishing permanent and close contact with the latter. The contact begins when the lists of enterprises are prepared that must be subjected to health regulations. The State Sanitary Inspector studies these enterprises through the sanitary-epidemiological centers. For that reason the State Sanitary Inspector must take care of the development and amplification of laboratory research of the sanitary-epidemiological centers organizing studies of the atmospheric air and improving the level of the staff of the sanitary-epidemiological centers.

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Considerations of The Feasibility of Control of Oxides of Nitrogen

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Recent research has indicated that the extent of ozone formation in the Los Angeles atmosphere is as much or more dependent upon nitrogen dioxide concentration as upon hydrocarbon concentration [11] [12] [14]. For this reason, suggestions have been made that work regarding control of oxides of nitrogen be started immediately. The urgency of this work is not due to consideration that oxides of nitrogen themselves might be approaching toxic concentrations; the levels involved [15] are much below the accepted toxic thresholds [1]. The advent of dangerous or near dangerous levels of ozone concentrations has provided much of the stimulus for considering control measures.

The major factors involving oxides of nitrogen which will be considered in this study are:

(1) Their role in ozone formation
(2) Nature and contribution of various sources
(3) State of present knowledge of control

The possible participation of oxides of nitrogen in formation of aerosols or eye irritating or crop damaging compounds will not be directly considered here. There has been, however, enough evidence of these roles [2] [13] [15] to give more impetus to considering control measures, although neither the nature of these compounds nor their mechanisms of formation has been defined.

Ozone Forming Reactions

The term *oxides of nitrogen* alone cannot be used in discussing chemical reaction mechanisms. This term includes N_2O, NO, NO_2, N_2O_4, N_2O_3, N_2O_5 and NO_3. Of these oxides, only NO, NO_2 (and its equilibrium product N_2O_4) and N_2O_5 have been seriously considered in studies of mechanisms of ozone formation.

The earliest theories of smog formation [20] regarded nitrogen dioxide (NO_2) only as a donor of atomic oxygen through a photochemically activated cycle,

$$NO_2 \rightarrow NO + O$$
$$NO + \tfrac{1}{2} O_2 \rightarrow NO_2$$

The presence of ozone was ascribed only to the reaction

$$O + O_2 \rightarrow O_3$$

Later work indicated that ozone could be readily produced by irradiating hydrocarbons in the presence of NO_2 [11] [12] [14] [28]. Stephens *et al.* [28] present a careful spectrophotometric analysis of this gaseous reaction mixture which shows definite presence of nitrogenous organic compounds of an unknown nature. This is evidence that there may be a direct reaction between NO_2 (or NO) and hydrocarbons in the free radical or stable state. This work also shows the formation of quantities of ozone in the same order of magnitude of amounts given in earlier work.

Recent Work on Atmospheric Mechanisms

Stephens [28] postulates that the nitrogenous material is formed by reaction between photochemically produced NO_2 and oxidation intermediates of hydrocarbons, and that NO_2 may be regenerated. Their paper also considers that nitric oxide (NO) may be directly involved in reaction with organic compounds, and not restricted to the expected role of being oxidized to NO_2.

When postulating chemical mechanisms it should be considered that both NO and NO_2 are unique in that they are stable free radicals. Any reaction which a single NO or NO_2 radical enters into with an ordinary molecule will result in a free radical being produced, and any reaction with another free radical will produce one or more stable molecules or two other free radicals, as

$$NO + A = F \text{ (or } F_1 + M_1)$$
$$\text{(or } A_1 + A_2, \text{ or } F_1 + F_2)$$

where A, A_1 and A_2 represent stable molecules and F, F_1 and F_2 represent free radicals. This consideration is important in terms of the photochemical nature of smog formation and in terms of some of the present hypotheses concerning atmospheric reactions [18] [25].

Littman *et al* [18] postulate that NO converts to NO_2 in the presence of certain hydrocarbons and that ozone is formed from photolysis of nitrogen dioxide. It is clear here that some oxidant other than ozone would be the successful competitor in the reaction of NO to NO_2. Littman also found NO in *normal* air in quantities well in excess of those of NO_2, but no quantitative comparison data were given.

Relative Effects of Reducing NO_x and Hydrocarbon Concentrations

Hydrocarbon control measures have been vigorously adopted in the Los Angeles area in the last 5 years. What is generally considered to be a practical lower level of hydrocarbon emissions from stationary sources is being approached. Research and development work on organic emissions from vehicles is being accelerated to find a method of reducing the discharge by at least 80%. In view of the apparent role of NO_2 in ozone formation, an estimate must be made of the ozone reduction that might be expected if hydrocarbon concentration alone is reduced to 20% of the present level.

Haagen-Smit [14] has presented an idealized curve which relates the amount of ozone which can be expected to form after 4 hr. of irradiation with various initial hydrocarbon (3-methylheptane) and NO_2 concentrations. Hydrocarbon and NO_2 concentrations used were generally of the same order of magnitude as exist in the Los Angeles atmosphere during

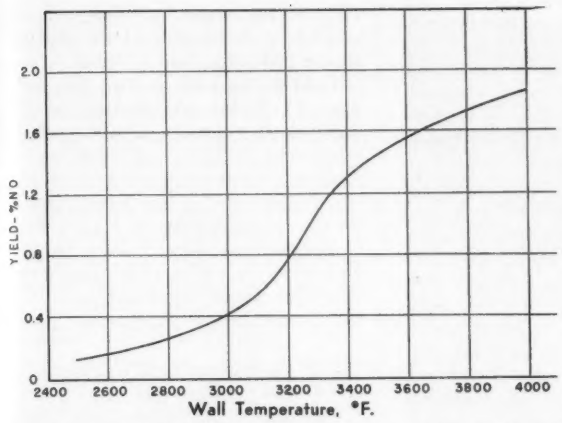

Fig. 1. Actual nitric oxide yield vs. wall temperature from a 40 ton I day equivalent 100% nitric acid furnace. (From E. D. Ermenc[7]).

heavy smog periods; that is, in the range of ½ to 1 ppm. This curve indicates that an equal percentage decrease of either contaminant would be equally effective in reducing ozone concentration, if initial hydrocarbon concentrations were ½ of the initial NO_2 concentrations. This ratio is approximately what is experienced in the Los Angeles area at present.

This graph would indicate that an 80% reduction in hydrocarbons alone would be quite satisfactory at present in reducing the ozone content. Haagen-Smit claims, however, that even if the hydrocarbon levels could be reduced 80% at once, the rapidly increasing automobile registration and corresponding gasoline usage and refining would bring the hydrocarbon concentration gradually toward present concentrations. With constantly rising NO_2 concentrations the overall effect would be to bring the ozone-forming capacity of the mixture even more rapidly back to present levels. Haagen-Smit urges that both hydrocarbons and oxides of nitrogen be controlled. The above paper is the only reference found which presents a quantitative statement as to the relative ozone forming potentials of mixtures of hydrocarbons and NO_2.

Sources of Oxides of Nitrogen

Assuming that it will be necessary to reduce oxides of nitrogen, what methods might be used? What are the major sources, and what concentrations of oxides are emitted from each? Estimates of emissions from the principal sources in Los Angeles County are given in Table I[4] [19].

No significant amount of oxides of nitrogen comes from nitric acid manufacture or use in most urban areas. Essentially all is the result of nitrogen fixation in combustion processes, according to the equilibrium.

$N_2 + O_2 = 2\ NO$. Extensive study of this equilibrium has been made by Gilbert and Daniels[6] and Ermenc and co-workers[7] in connection with a type of gas or oil-fired nitrogen fixation furnace commonly called the Wisconsin furnace. The studies were initiated originally to determine the feasibility of nitric acid manufacture using a furnace for fixation. The references show experimentally and theoretically determined reaction rate constants for formation and decomposition of nitric oxide between 1800°K and 2700°K. *Fig. 1* shows actual NO yields obtained from the furnace with different wall temperatures which were estimated to be about 300°F. less than combustion space temperatures.

The Effects of Temperature

Examination of the data contained in the above references[6] [7] shows the trends expected from thermodynamic consideration of the reaction. The rates of reaction of both the fixation and the reverse (decomposition) reaction increase rapidly with temperature. The decomposition rate constant is from about 150 to 8000 times the rate of formation constant in the temperature range of 4400°F. down to 2800°F. Equilibrium concentrations of NO increase with higher temperatures.

High temperatures and quick cooling of flue gases are both required for high yields of NO. Thermodynamically, lower temperatures would decrease the equilibrium concentration of NO, but under 1000°F. the decomposition rate is reduced to insignificance[4].

Concentrations of oxides of nitrogen from automobiles vary with engine acceleration rate. Idling and deceleration cycles emit about 20 ppm.; cruising, about 1500 ppm.; and acceleration, up to 4000 ppm.[19]. High concentrations can be explained by high cylinder flame temperatures (to 5500°F.)[22] and fast cooling rates. Analysis of exhausts with engines equipped with afterburners have shown little difference in total oxides content[21].

Steam generators in power plants emit higher concentrations of nitrogen oxides than do small boilers or heaters[19], again reflecting the effect of higher flame temperature (3000°F.) and perhaps rapid cooling due to use of economizers and better heat transfer apparatus.

The Effects of Excess Air

A third variable in combustion processes, excess air, will also determine the final concentration of nitrogen oxides. The equilibrium expression for the decomposition reaction, $2NO = N_2 + O_2$,

$$K_E = \frac{(pN_2)\,(pO_2)}{(pNO)^2}$$

, indicates that the equilibrium concentration of NO in the reaction is proportional to the square root of the effective concentration of oxygen present in the reaction mixture. Similarly, the rate of the fixation reaction,

$R_f = (pN_2)\ (pO_2)$, indicates that the rate should be directly proportional to the effective oxygen concentration. This relationship is shown by Daniels and Gilbert[6].

Excess air is an important factor in another reaction that occurs in combustion equipment as exhaust gases are cooled from about 600°F.

TABLE I

Source	NO_x concentration (ppm.)	Tons/day (as NO_2)
Vehicles	20-4000	770
Power Plants (gas and oil-fired)	400- 700	210
Other Boilers & Heaters	100- 500	120
Incineration	50- 150	20
	Total	1120

to atmospheric temperature. This reaction, $NO + \frac{1}{2} O_2 = NO_2$, gives higher equilibrium NO_2 yields at lower temperatures. But the rate of reaction is more rapid at lower temperatures because this is one of the rare termolecular reactions. It has been calculated that the half-time for this reaction in the atmosphere (21% O_2) for 10 pphm. NO would be 1000 hr. at room temperature[19]. Reaction rates would apparently be lower in warmer engine exhaust systems and with higher NO content, but no quantitative automotive data have been published regarding the extent of this oxidation. Unpublished and tentative analyses by the Los Angeles County Air Pollution Control District of auto exhausts in idling and deceleration cycles indicate that the greatest portion of total oxides is nitric oxide. The analyses also indicate that N_2O_5 or nitric acid aerosol is also measurable in the comparable order of magnitude of concentrations of NO_2.

Naturally Occurring Oxides of Nitrogen

There has been some contention that a substantial amount of oxides of nitrogen, particularly NO_2, is present in the atmosphere of the Los Angeles area due to natural causes. Whereas nitrogen fixation is known to occur from lightning discharges, there is substantial evidence that the great part of oxides of nitrogen found in this region is not due to any but artificial causes.

Possible Methods of Control

There are essentially no data in the literature relating to actual control of oxides of nitrogen in the low concentration ranges that must be considered here. Nevertheless, all known general control methods should be examined. Such methods include:

- Absorption in a pure liquid or solution,
- Adsorption on a solid,
- Changes in design or operation of combustion chambers or exhaust systems,
- Vapor phase reaction and subsequent collection,
- Changes in fuel,
- Catalytic decomposition of nitric oxide.

The well-known incineration method of control of oxidizable gases is not applicable here. Each of the above methods will be considered.

Absorption

A large amount of research has been done on absorption of soluble gases in water or aqueous solutions. Most of the work involves acid gases or ammonia. Recent work of Peters & Holman[24] and Peters[23] has considered efficiencies of collection of NO_2 in water and aqueous NaCl and NaOH solutions by use of a variety of absorption tower packings. The experiments of Peters indicate that relatively enormous amounts of water would be necessary to absorb appreciable amounts of NO_2 in concentrations below 2000 ppm. Peters and Holman indicate that for temperatures below 100°F. there is no appreciable difference in absorption of NO_2 between 20% NaOH solutions and pure water. Chambers and Sherwood[3] have indicated that NaOH solutions actually give poorer removal efficiencies.

The above work considers only NO_2. No reference was found that deals with efficiency of aqueous solutions or pure water in absorbing NO. It would be expected that NO, being only slightly soluble in water (7.34 ml./100 ml. water at 0°C.), and being neutral, would be absorbed only slightly by pure water, or acidic or basic solutions. However, NO reacts with certain salts, *i.e.* FeS to form solid compounds[16].

One other problem is involved in the use of an absorbing medium, that of regeneration, neutralization, or disposal of the medium. Dissolved NO_2 can be neutralized, but NO cannot. Either could, theoretically, be combined with other reacting material.

Adsorption

The very high efficiency of adsorption of small concentrations of certain gases on activated solids such as silica gel or activated carbon is well known. Charcoal, particularly, is in general use as an adsorbent for toxic and other gases. Littman used charcoal to collect NO_2 (and organic nitrites) while the charcoal passed NO[18]. No better adsorber than charcoal (or treated charcoal) is known for most gases.

Ermenc[8] has recently published operational and design details of a pilot plant to convert NO from a Wisconsin furnace to NO_2 and thence to nitric acid. Furnace gases containing on the order of 1.5% NO are dried, the NO oxidized using silica gel as catalyst, and the gases containing NO_2 are cooled to 10°F. The dilute NO_2 is adsorbed in silica gel, desorbed by heating, and the concentrated NO_2 absorbed in water.

Considerable work has also been done by Foster and Daniels on efficiencies of a variety of silica gels in adsorbing NO_2[9]. Efficiencies as high as 99% have been reported with low velocities of a flue gas stream at 25°C. containing about 1.15% NO_2. Using the data of the latter reference, Peters[23] showed a wide range of efficiencies which increased as:

(1) the temperature was lowered,
(2) the contact time was raised,
(3) the pressure was raised,
(4) the cycle time was decreased.

Efficiency decreased to ½ when the temperature was raised from 15°C. to 25°C. Efficiency was decreased to ⅓ when the cycle time was tripled. A reduction of entering NO_2 content from 1.0% to 0.2% (2000 ppm.) resulted in reducing the collection efficiency to half.

Foster and Daniels[9] used a catalyst to oxidize NO to NO_2 before adsorption, but reported that the collection medium, silica gel, itself had some ability to catalyse oxidation to NO_2, particularly in the presence of water and NO_2.

The problems involving use of solid adsorbents do not end with the development of a highly efficient adsorbing process. Unless the adsorbent is to be immediately discarded, NO_2 will have to be desorbed (most effectually by heating) and collected in another manner, as by absorption. An absorption process at this point will not present the very difficult problems discussed in the above paragraphs on absorption because the NO_2 concentrations from a desorption process would be considerably greater[9].

Both absorption and adsorption present 2 similar problems. For effective collection, both methods must be carried out at low temperatures and final disposal must be considered. It appears also that large amounts of collection media would be required, along with considerable size of equipment, to gain efficient collection. The latter difficulties would be magnified in designing collection systems for mobile sources.

Control by Changes in Design or Operation of Sources

Changes in design of combustion equipment or its operation, or changes in fuel must be considered

as possible control methods. This possibility is outlined by Connelly and Nobe[4] in a report which deals with oxides of nitrogen emission from a gas-fired domestic hot water heater. The report contains a review of some of the thermodynamic problems involved in reducing oxides emission by use of the decomposition reaction,

$$2\,NO = N_2 + O_2$$

Daniels[4] states that from 1300 to 2000°F. decomposition is catalyzed by the walls of the exhaust system, but that from 2000 to 2500°F. it is a homogeneous gas phase reaction. No work has been reported on development of a catalyst for low temperature decomposition. Also, no development is known of designs intended to maintain flue gases for longer times at elevated temperatures to allow decomposition to occur.

Lower flame temperatures may also be considered as reducing the amount of nitrogen fixation. Unfortunately, reducing flame temperature in work producing equipment as power plant boilers or automotive engines reduces thermodynamic efficiency. Nevertheless, such a procedure would greatly reduce the amount of NO emitted, other conditions being equal. Another factor in reducing fixation would be lowering the amount of excess air used in burning, but this amount is almost irreducible in stationary sources. In the automobile industry the tendency has been to increase the excess air used, but only slightly.

Control by Vapor Phase Reactions

Vapor phase reactions of NO and NO_2 have been considered in control of oxides of nitrogen. In a review of the problem of formation by oxides of nitrogen of so-called *vapor-phase gums* in gas lines from manufactured fuel gas plants, Shnidman[27] describes several methods of control. One, regarding reaction with FeS, is mentioned above[16]; the other[10] [26], is a unique method and involves accelerating the reaction of NO, oxygen and *reactive* hydrocarbons present in manufactured gas by passing the gas stream through electrodes operating at a potential difference of about 10000 volts. This treatment rapidly accelerates formation of vapor phase gum and agglomerates the mist so it may be collected in a scrubber normally used to remove traces of naphthalene from the same gas stream. An electric treater built at the Philadelphia Coke Company plant

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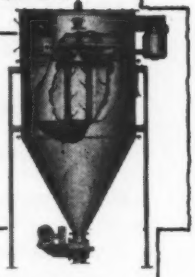

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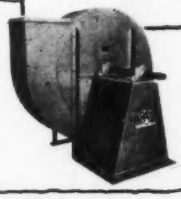

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in 1935 has removed 96-98% of the nitric oxide produced since that time. The application of this method to control emissions from stationary sources would appear to be worthwhile to investigate, but such application to control automotive engine exhaust would appear to be difficult.

Changes in Fuels

In combustion calculations involving fuel containing nitrogen gas or organically bound nitrogen in small quantities, these components have classically been considered to remain as or oxidize to nitrogen gas. There has been some speculation that nitrogen oxides in excess of the amounts that would be formed from atmospheric nitrogen fixation alone might result from the burning of fuel containing organic or other nitrogen.

Calculations show, however, that the ratio of concentrations of atmospheric nitrogen to organic nitrogen in a combustion chamber would be in the order of 500 to 1 for typical fuel oils. Considering also that such nitrogen would originally exist in a reduced state, it does not seem likely that bound nitrogen in fuels would materially increase the fixation of nitrogen in combustion chambers. Tests have shown that concentrations of oxides of nitrogen from oil-fired power plant boilers are only slightly greater than from similar gas-fired boilers[19]. The small difference may be due wholly to higher flame temperatures when burning oil. For these reasons, there would seem to be no advantage in removing nitrogenous compounds from fuels.

Catalytic Decomposition of Nitric Oxide

Theoretical and experimental data referred to in preceding paragraphs show rates of decomposition of NO in flue gases at high temperatures. The use of a heterogeneous or homogenous catalyst cannot, of course, change the equilibrium concentrations involved in the decomposition reaction. Theoretically, use of catalysts in contact with gases during cooling would allow the reaction to reach equilibrium conditions more rapidly, but no experimental work along this line has been reported. Research involving this reaction has been mainly devoted to *freezing the equilibrium* by rapid cooling in order to prevent decomposition. The former area of research would seem to be worth pursuing.

Conclusions

There is no ready solution for control of oxides of nitrogen as a general atmospheric contaminant. No practical methods have been devised, and theoretical considerations indicate that much experimental work must be done before any development of successful devices is accomplished. It cannot be said here that it is not feasible to control nitrogen oxides; feasibility would depend upon how urgently control is needed. But if control is found to be necessary, research will be necessary.

Considering work so far done on the role of NO_2 or NO in ozone formation, it cannot be definitely stated whether organic materials or oxides of nitrogen are the limiting factors in ozone formation.

More evidence of necessity of control of nitrogen must be presented before control systems can be legally required. On the other hand, research on control methods up to final development stages should not wait for absolute justification.

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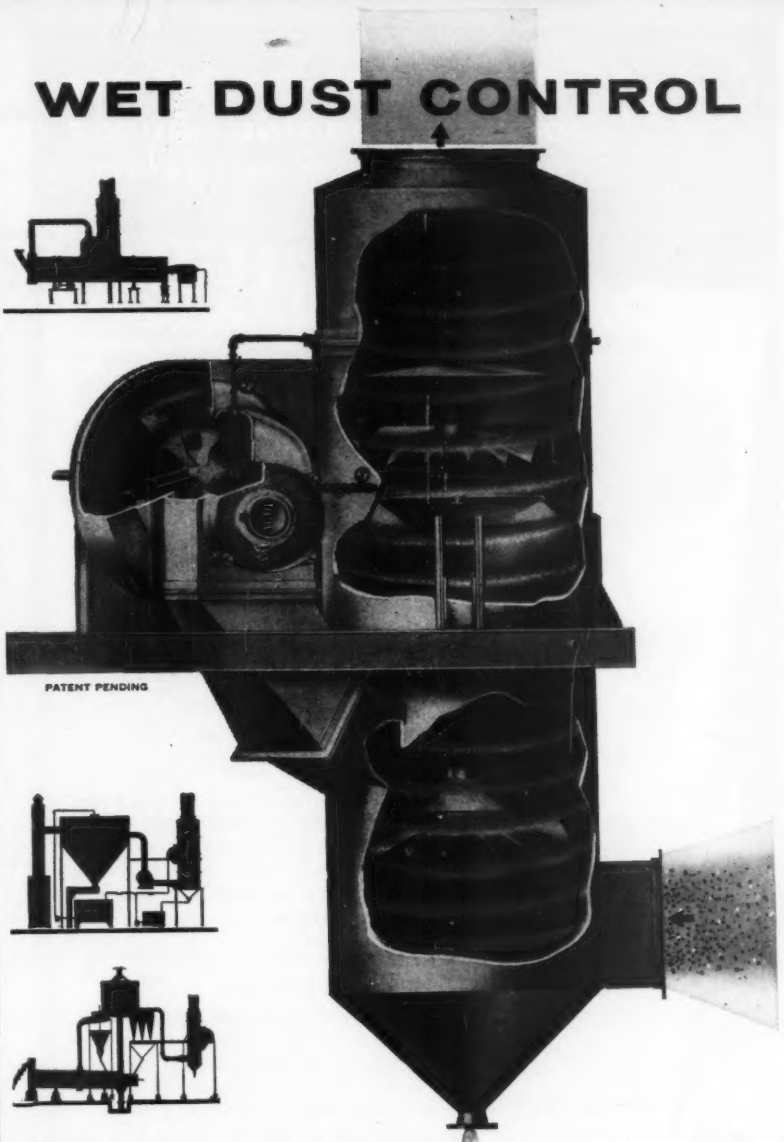

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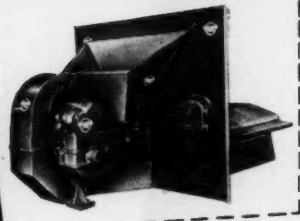

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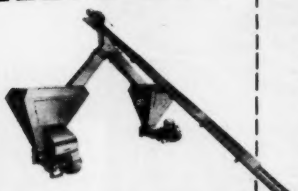

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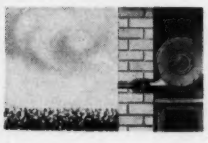

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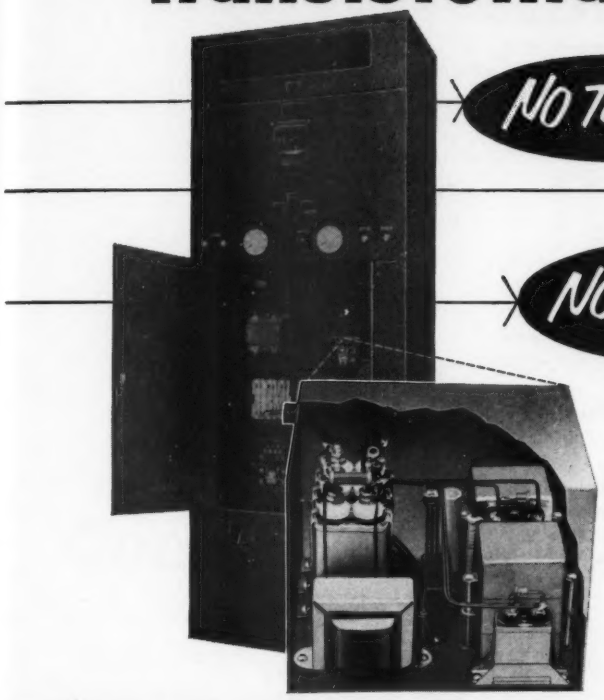

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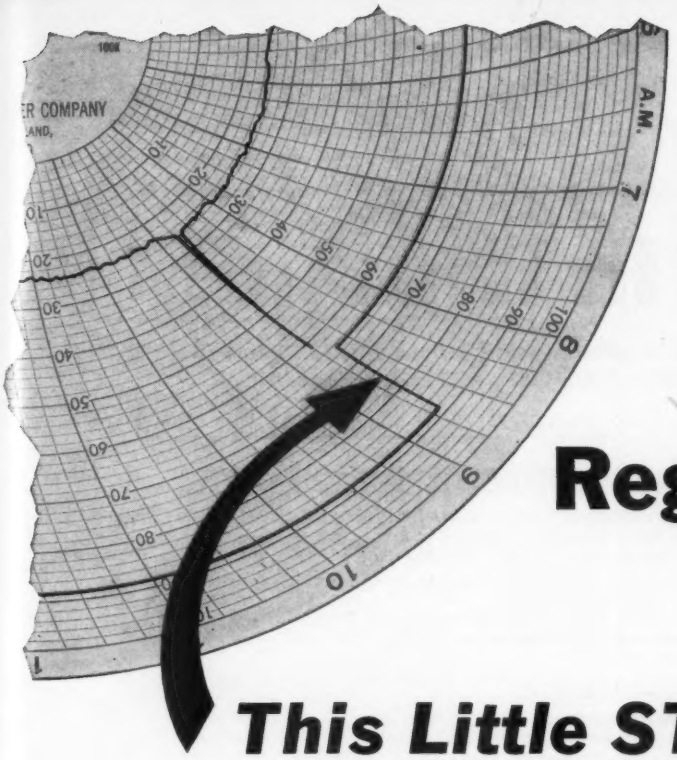

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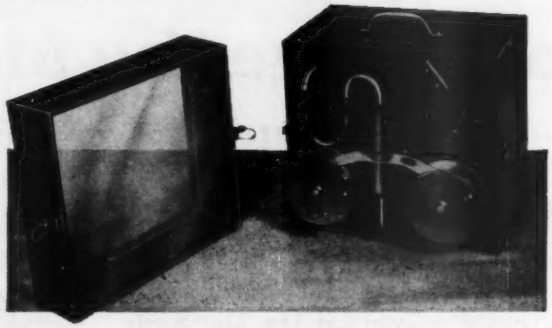

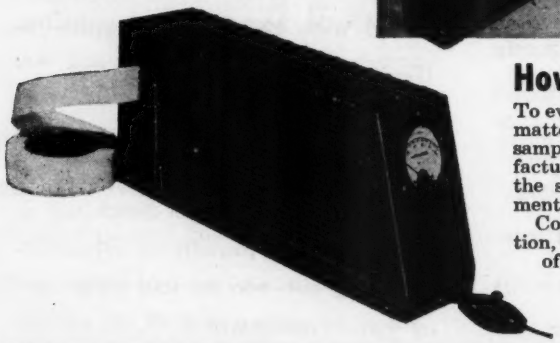

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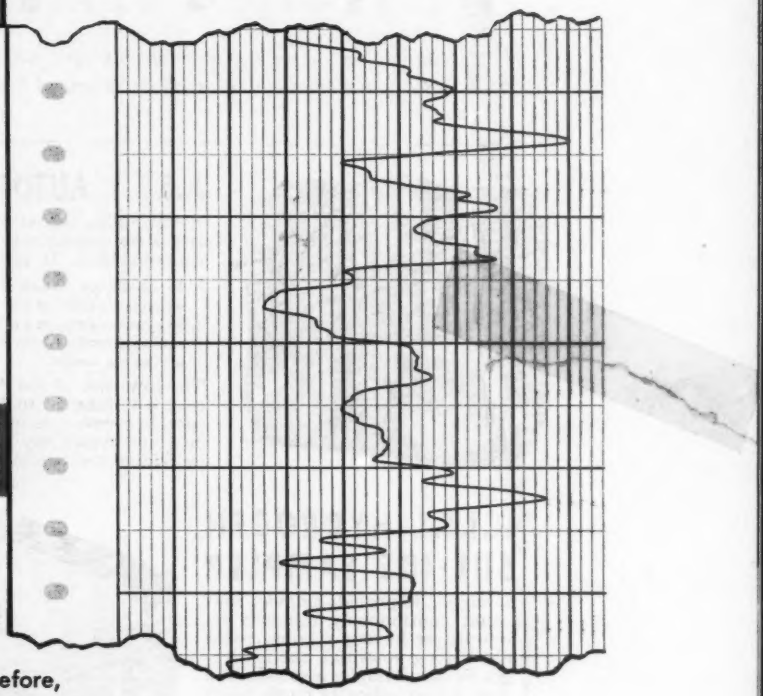


high resolution recording system

Sliced up thinner than ever before, the wind can record itself with a new maximum of resolution in the Beckman & Whitley Type F System. This not only permits a more intimate documentation of the features of the winds, but, even where detailed records are not required, offers many advantages for fixed-station and system-telemetering uses.

Operating from standard 115-volt 60-cps supply, the Type F can be used in portable applications where the increased resolution is needed, by the addition of an accessory battery-operated power supply.

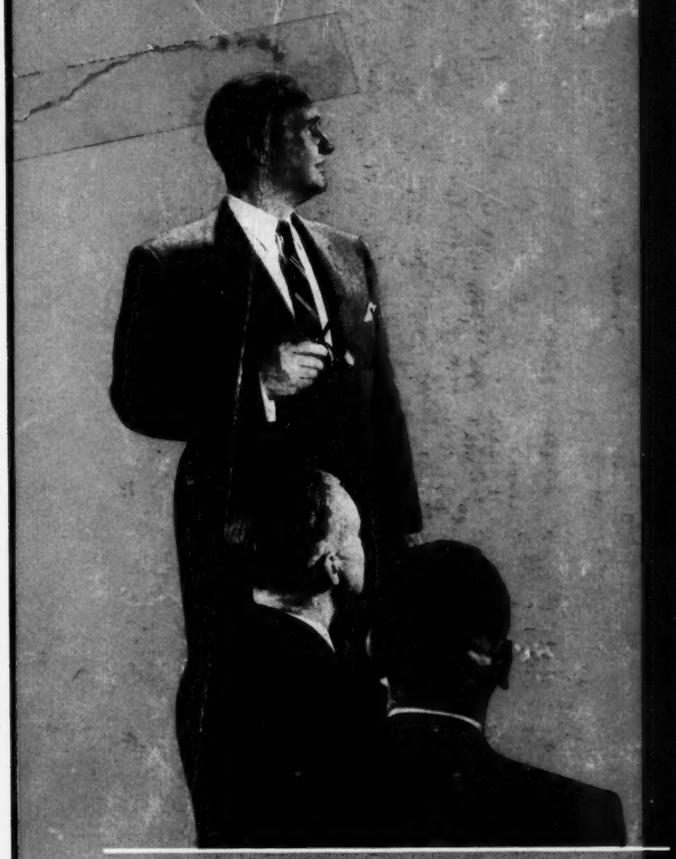
Sample chart illustrated, produced by typical recorder shown, reveals fine, smooth detail recorded where maximum chart width is six miles per hour at a chart speed of 6-in. per min. Translator unit, designed for either bench-top or rack mounting, permits instantaneous switching between the four scales calibrated to maxima of 6, 12, 30, and 60 miles per hour.

For further information write:

Beckman & Whitley INC.

SAN CARLOS 4, CALIFORNIA

Research-Cottrell 1956 Orders for 20 Central Station Precipitators



Consolidated Edison Company
STATION: ASTORIA • UNIT NUMBER: 3

Consolidated Edison Company
STATION: ARTHUR KILL • UNIT NUMBER: 2

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